

Comparative Corrosion Behavior of Carbon Steel and High Chromium Steel Nanoparticles

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ABSTRACT

The electrochemical activity of carbon steel and high chromium steel nanoparticle (HCS) in 0.1 M HCl as well as in 0.1 M NaCl was studied using the atomic force microscopy (AFM) and Kelvin probe force microscopy (KFM). The corrosion processes occurring at the nanoparticles lead to decrease in the size and the surface potential of carbon steel nanoparticles with increase in time. The change in the shape and size of the nanoparticles in AFM and KFM mapping showed that the corrosion occurred due to the oxidation reaction at the anode. However, the corrosion at carbon steel surface occurred more severely than high chromium steel nanoparticle in both the medium. The decrease of the surface potential and the size of carbon steel nanoparticle were more than the high chromium steel nanoparticle. This was because of the higher corrosion resistance of high chromium steel nanoparticle. The formation of protective film on the high chromium steel nanoparticle surface suppresses the electrochemical activity. It was proved that high chromium steel nanoparticle showed better corrosion protection performance than carbon steel nanoparticle both in 0.1 M HCl and 0.1 M NaCl.

Keywords: AFM, KFM, Nanoparticles, Corrosion, Carbon steel, Chromium steel.

INTRODUCTION

Metal nanoparticles possess excellent electronic, optical and structural properties whereas the bulk solids do not have these properties. Therefore, the importance of nanoparticles in pharmaceuticals, environmental detection and monitoring, catalysis, biological applications and information storage was well known [1-3]. The carbon tetrachloride and arsenic present in ground water are cleaned up by using pure iron and iron oxide nanoparticle respectively. The pigments, humidity sensors, dielectric ceramics and solar cells contain titanium dioxide [4-6]. Both qualitative and quantitative information on size, morphology, surface texture and roughness of nanoparticles are given by AFM. The characterization of size of nanoparticles in multiple mediums is done by AFM from 1 nm to 8 μ m. The AFM is providing spatial distribution information on composite materials. The imaging analysis and data processing are used to measure the statistics on group of particles. Mass distribution can be easily calculated with help of the material density.

The mapping of the change in surface potential between the tip and the sample is studied by

KFM. High-resolution mapping of the distribution of the surface potential on conducting and non-conducting samples can be obtained by AFM and KFM. KFM was used to measure the potential difference between AFM tip and the sample. Mapping the work function of the sample with high spatial resolution was done by KFM. The electronic properties of chalcopyrite solar cell materials have been investigated [7]. The measurement of surface potential with better spatial resolution of few nanometers is measured by analyzing the Coulombic force between AFM tip and sample in KFM. KFM has also been used to study. On the other hand, the electrical properties of both biological materials as well as organic materials has been investigated [8-10]. The use of KFM in imaging potential distributions on the surface of nanoparticles makes the KFM the best technique for characterization of the electrical properties of nanostructures. The potential measurements were done in KFM to study the corrosion behavior of the nanoparticle [11-15]. The quantity of the measured electric potential depends on the size of the nanoparticle and the geometry of the probe and knowledge of the contrast transfer mechanism in KFM. The

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knowledge of the will permit the combination of data which is likely to significantly facilitate The improved characterization of corrosion analysis was done by knowing the contrast transfer mechanism with the help of electric potential data and high-resolution surface topography.

In this project, the surface topographic images and surface potential of carbon steel and high chromium steel nanoparticles (mass %:22Cr-9 Ni-7Mn-Fe) in 0.1 M NaCl as well as 0.1 M HCl are investigated by AFM and KFM. The nanoparticle was also analyzed with different processing time in 0.1 M HCl as well as in 0.1 M NaCl solution with respect to their size and surface potential.

EXPERIMENTAL

The average nanoparticle size of carbon steel and high chromium steel respectively were 1500 ± 300 nm and 1500 ± 300 nm. The dispersion of nanoparticles were done in 0.1 M HCl and 0.1 M NaCl containing ethanol and stirring for 2 h.

AFM and KFM evaluated the surface morphology of the nanoparticles. The AFM analysis was done in tapping mode with a $20 \mu\text{m}$ scanner. The experiments were conducted thrice on different samples for ensuring the validity of the measured data. KFM measured the surface potential of the nanoparticle by applying a modulation bias voltage of 25 kHz, 1V, between the probe tip and the sample. The amplitude detection mode with noncontact mode was used during the KFM imaging process in AFM operation.

In KFM, the scanning of the sample is done with Pt-coated Si tips by using the standard contact mode of AFM set up. The schematic representation of a KFM experimental apparatus was shown in Figure 1. The Frequency Modulation (FM) mode of AFM system for topography measurement is at the lower part and the components for surface potential mapping with KFM controller and lock-in amplifier are at the upper part. The low and high frequency signals are filtered by a band-pass filter.

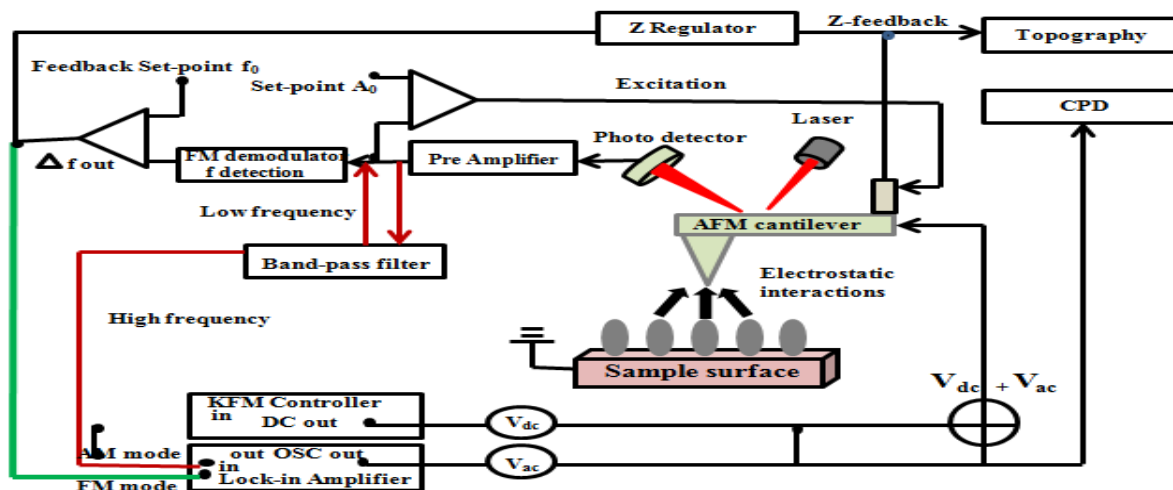


Figure1. Schematic representation of AFM and KFM system.

RESULTS AND DISCUSSION

Effect of 0.1 M HCl on Carbon Steel Nanoparticles

Corrosion processes occurring at the nanoparticle are studied by AFM and KFM in 0.1 M HCl solution. The surface potential generally is the average value on the entire surface of a nanoparticle. The surface of the nanoparticles contains both the regions of anode and cathode and hence there is no uniformity in the local potential. Hence, knowing the local potentials helps to understand and analyze the corrosion processes. Figure 2 shows the topographic images and their distribution of surface potential on the carbon steel nanoparticle in

0.1 M HCl for various processing time. Carbon steel nanoparticles were treated with 0.1 M HCl solution in different processing time and imaged topographically by AFM and KFM on Platinum surface. In AFM, the globular shape of nanoparticle is produced during the mapping on the surface of the nanoparticle and size of the nanoparticle is decreased with increase in test time in acidic solution. The decrease in the size of the nanoparticle from 1100 nm at 1 h to 700 nm at 5 h is due to the degradation of nanoparticle. On the other hand, the decrease in the value of surface potential of the nanoparticle is from 150 mV at 1 h to 40 mV at 5 h. This shows the increase in the rate of corrosion of carbon steel nanoparticle in acidic solution.

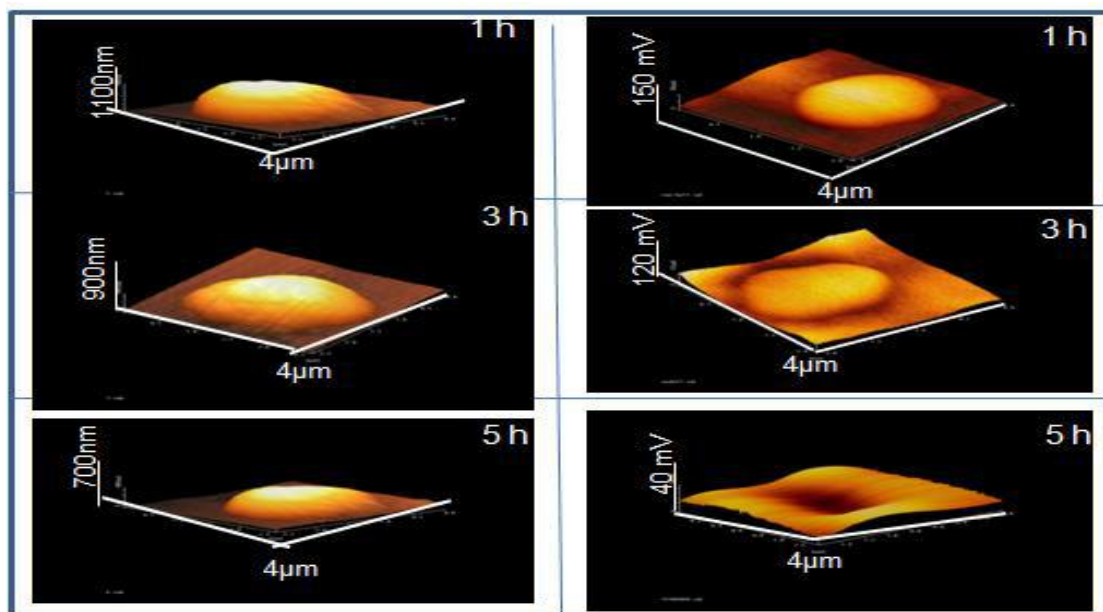


Figure2. AFM (left) and KFM (right) images of carbon steel nanoparticle treated in 0.1M HCl at different hours.

The maximum height (H_{max}) of AFM and the peak potential (V_{peak}) of KFM for the carbon steel nanoparticle corresponding to line profile diagram of AFM and KFM images are depicted in Figure 3a and 3 b respectively for the carbon steel nanoparticle in acidic solution. The size of the AFM image curve becomes reduced with time. On the other hand, there is a reduction in

the potential peak of KFM with time. The decrease in potential and size of the nanoparticle shows that corrosion takes place in the acidic medium. The slow change in W_{max} and H_{max} in AFM and fast change in surface peak potential (V_{max}) in KFM takes place with time. The occurrence of severe corrosion of carbon steel nanoparticle is shown in KFM.

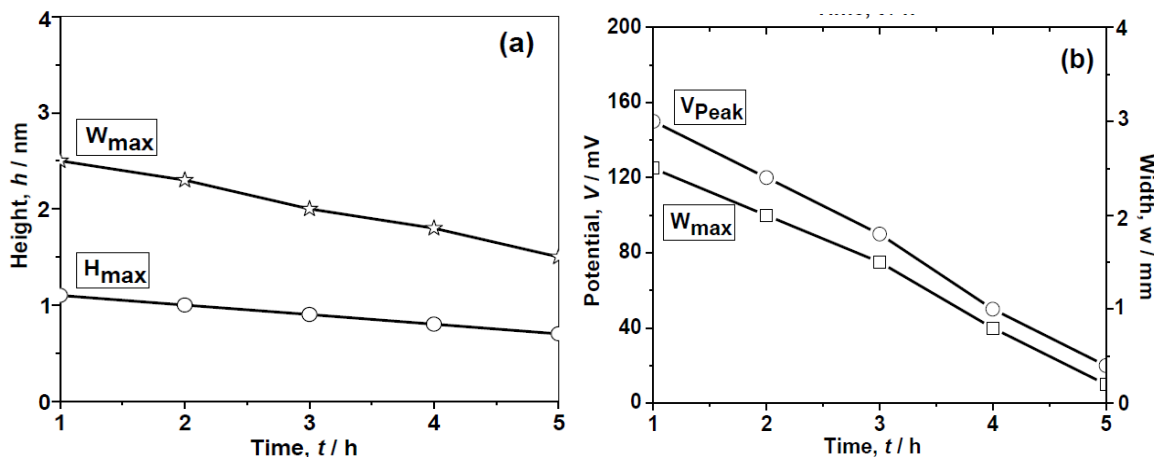


Figure3. Line scans from AFM and KFM images of carbon steel nanoparticle treated with 0.1M HCl containing ethanol at different hours (a) the maximum height (H_{max}) and (b) the peak potential (V_{peak}).

Effect of 0.1 M NaCl on Carbon Steel Nanoparticles

The distribution of potential and topographic surface of carbon steel nanoparticle in various hours of 0.1 M NaCl is shown in Fig. 4. The decrease in size of the carbon steel nanoparticle is from 1200 nm at 1 h to 800 nm at 5 h. At the same time, the decrease of potential is from 150 mV at 1 h to 80 mV at 5 h. The effect of 0.1 M NaCl on surface potential is significantly visible as there is an increase in the test time. The

increase in the degradation of carbon steel nanoparticle is shown by the corresponding decrease in the potential with increase in test time. The change in size of the nanoparticle with time leads to the reduction in the tip potential. This is due to the degradation of sample with increasing test time. The flattening of KFM image starts at the third hour and ends up with the image of like bowl at the fifth hour. This is because of the higher corrosion rate of carbon steel nanoparticle. The lower value of surface

potential shows that carbon nanoparticles with increasing test time are highly corroded.

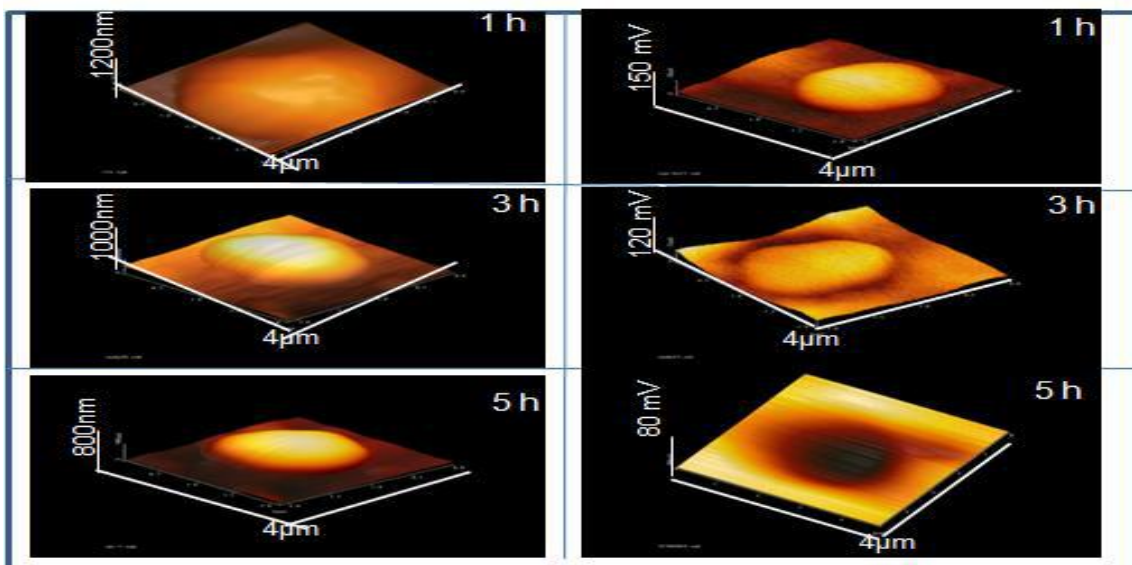


Figure 4. AFM (left) and KFM (right) images of carbon steel nanoparticle at different hours in 0.1 M NaCl solution.

The height (H_{max}) of AFM and the peak potential (V_{peak}) of KFM for the carbon steel nanoparticle corresponding to line profile of AFM and KFM images in 0.1 M NaCl are presented in Figures 5(a) and (b) respectively. It is evident from the figures that the nanoparticle size and its potential become reduced with increase in time. The corrosion of nanoparticle leads to change of peak potential curve after

third hour testing time. This leads to the decrease of surface potential of carbon steel nanoparticles because the NaCl increases the degradation of nanoparticle. The strong reduction of surface potential peak, V_{peak} , with increase in test time indicates the sensitivity of KFM to the electrochemical activity of carbon nanoparticles.

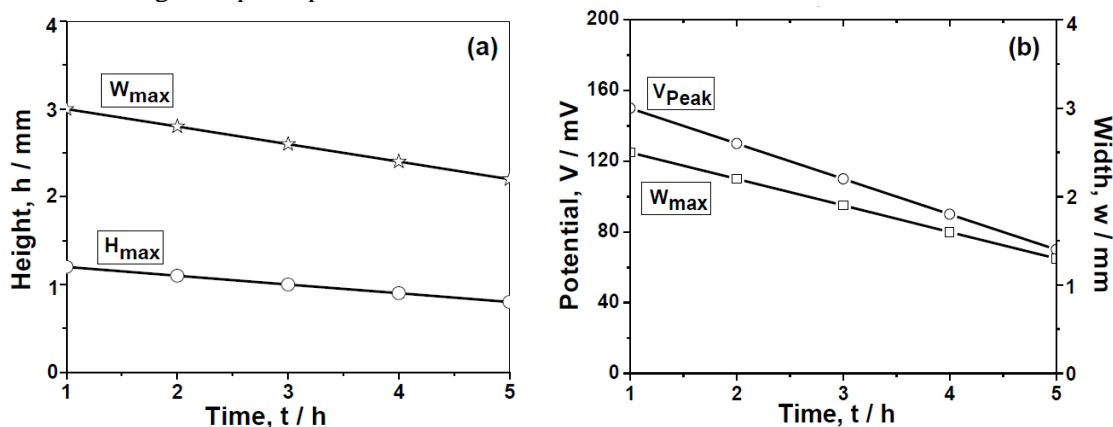


Figure 5. Line scans from AFM and KFM images of carbon steel nanoparticle treated with 0.1M NaCl containing ethanol at different hours (a) the maximum height (H_{max}) and (b) the peak potential (V_{peak}).

Effect of 0.1M HCl on High Chromium Steel Nanoparticles

The shape and potential distribution of high chromium steel nanoparticle in 0.1 M HCl for different hours are presented in Figure 6. Globular shape of AFM image is produced by mapping of high chromium nanoparticle and maintains the constant shape even after 5 hours of testing. The surface potential ranges from 150 mV at 1 h to 90 mV at 5 h. The higher surface potential of high chromium nanoparticle than

that of carbon nanoparticle after 5 h shows that the corrosion resistance of high chromium steel nanoparticle is higher due to the deposition of corrosion product film on the nanoparticle surface. Moreover, the surface potential of high chromium steel decreases slowly compared to carbon steel nanoparticle. The formation of chromium oxide protective film on high chromium steel nanoparticle causes the higher corrosion resistance of high chromium steel nanoparticle.

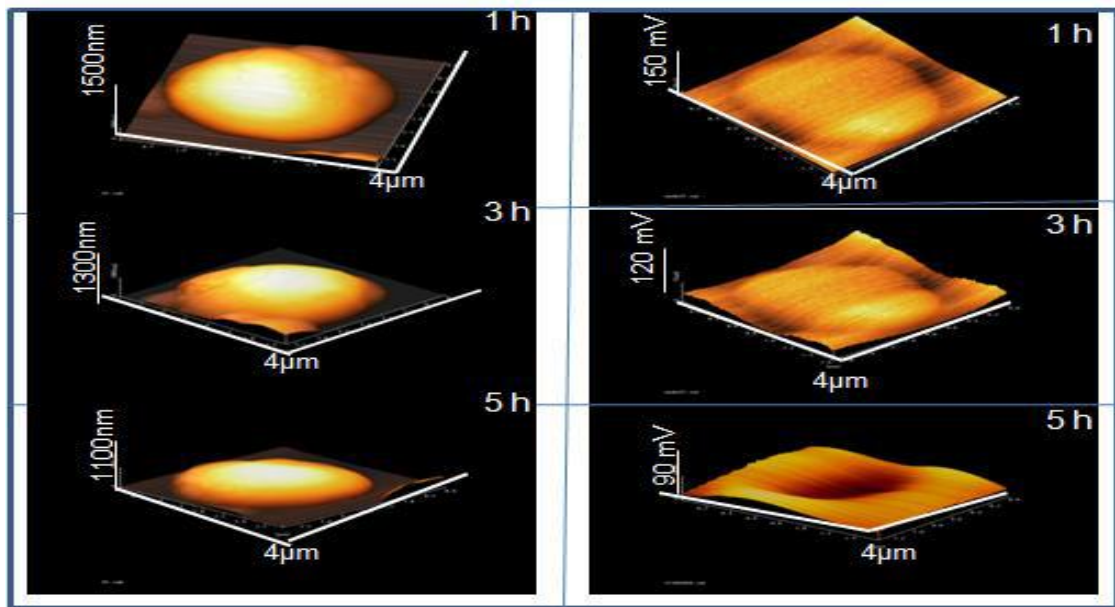


Figure6. AFM (left) and KFM (right) images of high chromium steel (HCS) nanoparticle in 0.1M HCl at different hours.

The height (Hmax) of AFM and the potential peak (Vpeak) of KFM corresponding to Line profile of AFM and KFM images of high chromium steel nanoparticle in 0.1 M HCl at different hours are shown in Fig. 7 (a) and (b) respectively. The slow change in size and its potential of the chromium steel nanoparticle with time in 0.1 M HCl solution is due to higher corrosion resistance of high chromium steel

nanoparticle. The reduction in potential and size of high chromium nanoparticle is comparatively lower than that of carbon steel nanoparticle. This is because of the deposition of chromium oxide protective film on high chromium steel nanoparticle that hinders the corrosion of nanoparticle. Hence, it is concluded that the corrosion process occurs very slightly at high chromium nanoparticle in 0.1 M HCl solution.

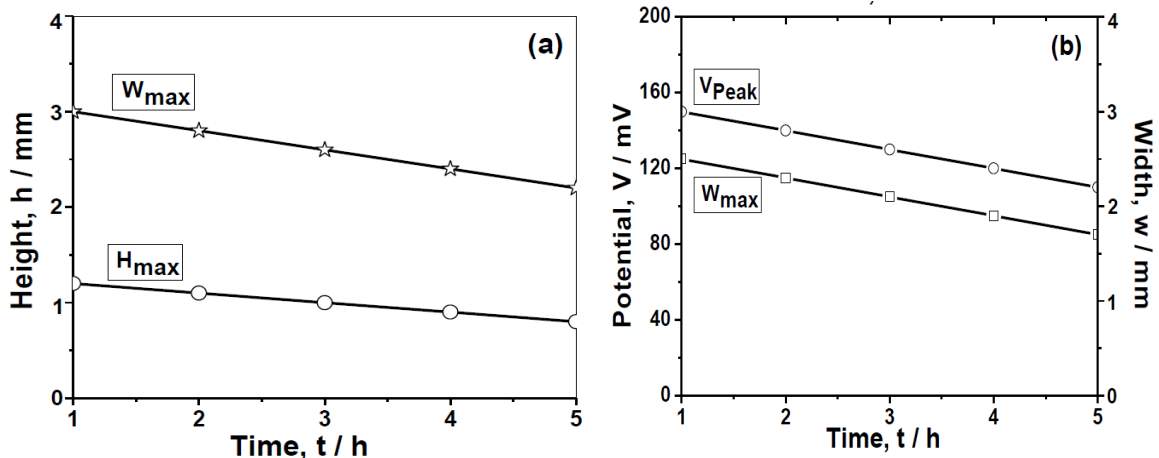


Figure7. Line scans from AFM and KFM images of iron nanoparticle treated with 0.1 M HCl containing ethanol at different time. (a) the maximum height (Hmax) and (b) the peak potential (Vpeak).

Effect of 0.1M NaCl on High Chromium Steel Nanoparticles

Figure 8 depicts the shape and potential distribution of high chromium steel nanoparticle in 0.1 M NaCl for different hours. The maximum height (Hmax) of AFM and the peak potential (Vpeak) of KFM corresponding to line profile of AFM and KFM images of high chromium steel nanoparticle in 0.1 M NaCl at different hours are depicted in Fig. 9 (a) and (b) respectively.

The slow reduction of the surface potential high chromium steel nanoparticle was the result of greater protection performance of high chromium steel nanoparticle. Hence, the deposition of protective film on the surface of high chromium steel nanoparticle reduces the degradation of the nanoparticle. It was concluded that high chromium steel nanoparticle possessed good resistance of corrosion both in 0.1 M NaCl solution as well as in 0.1 M HCl solution compared to carbon steel.

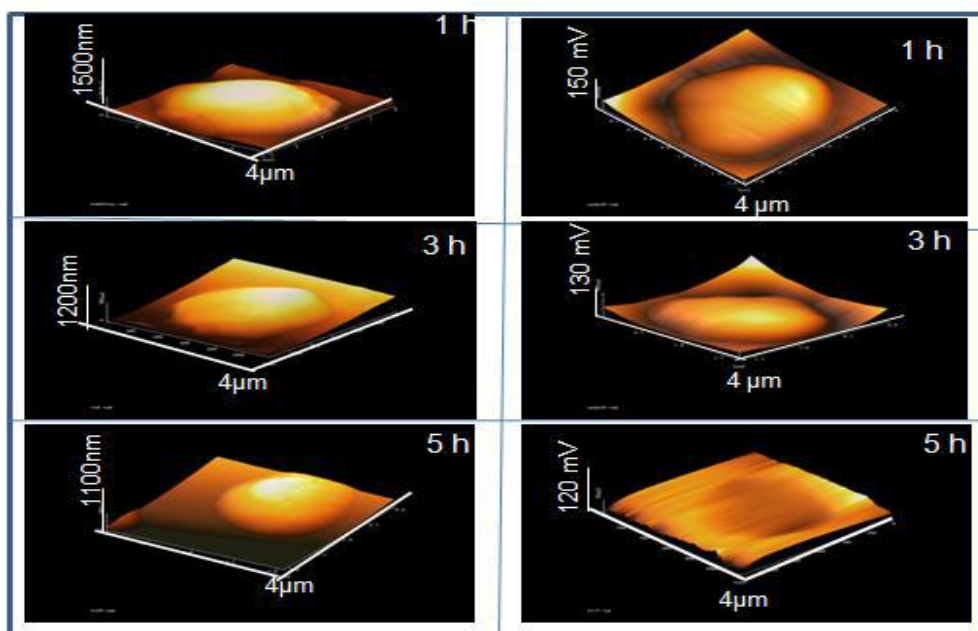


Figure 8. AFM (left) and KFM (right) images of high chromium steel (HCS) nanoparticle in 0.1M NaCl at different hours.

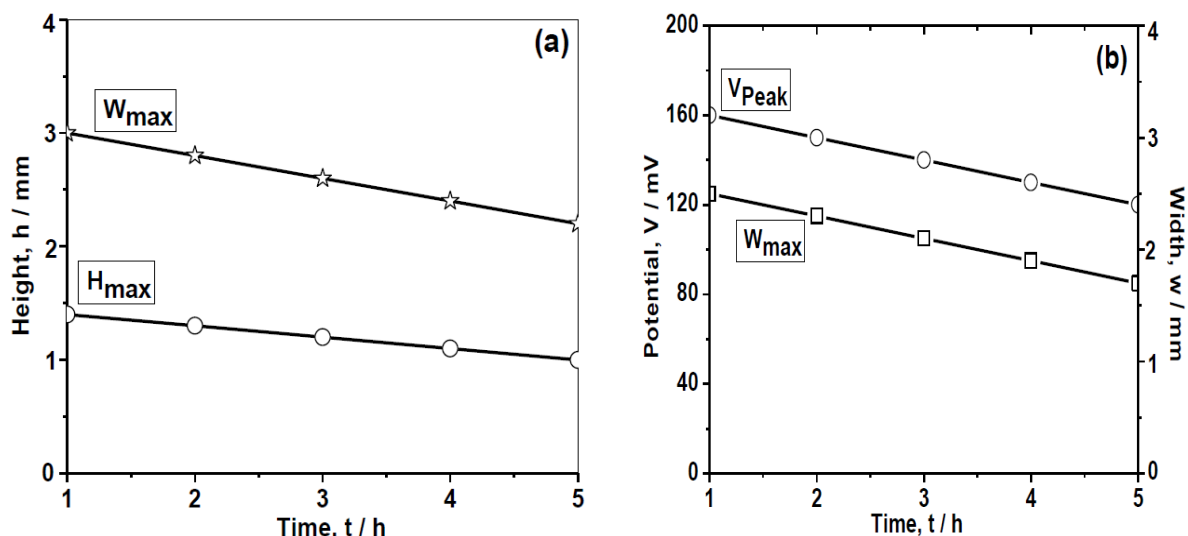


Figure 9. Line scans from AFM and KFM images of HCS nanoparticle treated with 0.1 M NaCl containing ethanol (a) the maximum height (H_{max}) and (b) the peak potential (V_{peak}).

CONCLUSION

The topographic images and the surface potentials of carbon steel and high chromium steel nanoparticles were measured. AFM and KFM investigated the relation between the topographic image and surface potential of nanoparticle. The decrease in shape and the surface potential of carbon steel nanoparticles with time in 0.1 M NaCl indicated the degradation of nanoparticles. Similarly, the reduction of surface potential of carbon steel nanoparticles occurs with increase in test time. On the other hand, no significant change in the surface potential of high chromium steel nanoparticles was found both in 0.1 M HCl solution as well as 0.1 M NaCl solution. The

slow reduction of surface potential of the high chromium steel nanoparticle compared to carbon steel nanoparticle was due to the deposition of protective film on high chromium steel nanoparticle. It was found that high chromium steel nanoparticle possessed better corrosion resistance both in 0.1 M NaCl and acidic solution compared to carbon steel nanoparticle.

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