

N.A. Al-Rubaiey

Petroleum Technology
Department, University of
Technology, Baghdad, Iraq.
100108@uotechnology.edu.iq

F.S. Kadhim

Petroleum Technology
Department, University of
Technology, Baghdad, Iraq.
fadhilkadhim47@yahoo.com

A.A. Ati

Nanotechnology and
Advanced Materials
Research Center, University
of Technology, Baghdad, Iraq
aliphysics1@gmail.com

Nano Ferrites as Corrosion Inhibitors for Carbon Steel in Local Iraqi Bentonite Mud

Abstract: Corrosion processes are accountable for serious losses in the oil industry. Although organic and inorganic materials and mixed materials inhibitors have been used for a long time to control or reduce corrosion. Using nano-materials as inhibitors has gained an increasing applications role because of their exceptional properties. Nano materials are good corrosion inhibitors because they possess many advantages such as high efficiency of inhibition, low cost, minimum toxicity and effortless production. This work examines the use of nano-materials as inhibitors to prevent corrosion of carbon steel in drilling mud. Anti-corrosion properties of zinc and nickel ferrite nano materials ($ZnFe_2O_4$, $Zn_{0.6}Ni_{0.4}Fe_2O_4$) have been investigated over carbon steel in local Iraqi bentonite mud as a source of the corrosion. It has been found that under the given conditions, ferrites act as efficient corrosion inhibitors of carbon steel.

Keywords- Bentonite, carbon steel, corrosion, ferrites, inhibitors, nanotechnology.

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1. Introduction

Nanotechnology is the field of discipline that deals with materials in the range of nanometers. In the past years, an enormous deal of progress has been achieved in this subject. It has also been used as a tool and technology in a wide range of applications such as medicines, electronics equipment and composite materials. It becomes achievable now to design, manufacture and operate nanomaterial with exceptional mechanical, optical and magnetic properties. Nanomaterial can be defined as a small object that possesses a complete unit, which has its own unique properties. As nanoparticles located in between macroscopic and bulk material, therefore it will have their sole properties and including small size, surface and quantum effects. The particles size is so small that different physical and chemical properties from the bulk material may be obtained.

Petroleum industry has taken the advantage of this technology by investing a lot of money and time to enhance and improve the efficiency of many fields such as exploration, drilling, reservoir protection, hydrocarbon recovery and processing [1-3]. This technology can definitely provide solutions to problems facing the drilling industry and improve performance to many oil and gas processes [4-7]. In petroleum drilling for example, nanotechnology has many applications such as in drilling fluid, drilling bit, down hole tools, cement and well logging. The potential of saving bore hole stability and reducing mud loss

is also investigated. Adding nano-particles can give special uniqueness to the base drilling mud, which makes it work in a complicated environment such as keeping the reservoir from formation damage [8].

In addition, some nanomaterial can help in removing corrosive materials such as ZnO and thus reducing corrosion and other environmental problems. Adding nanoparticles to drilling fluid also can reduce wear and tear of down hole tools by giving less abrasive force caused by the drilling aggressive environment. The use of nanoparticles for anticorrosion coatings has achieved significant attention and importance. Several researchers have shown nanoparticles to perform better and qualify them as a better alternative for anticorrosion coatings in composites and polymers [9].

2. Nature of Ferrite Nanoparticles

Nano ferrites are important magnetic materials because of their remarkable magnetic and electrical properties and possess high chemical and thermal stabilities. These nano-materials have been used in many applications. They can be prepared at different sizes using various techniques such as thermal decomposition, co-precipitation, micro emulsion, ball milling, and sol-gel [10]. They can be isolated in various fluid carriers after appropriate surface modification to make magnetic nano-liquid and surface change may be completed with surfactants. Configuration of tetrahedral and octahedral position of ferrite

adjusts the overall properties like electrical conductivity, resistivity, thermal conductivity and magnetic property.

In the present work, an attempt has been made to prepare and characterize nanoparticles of $ZnFe_2O_4$ and $Zn_{0.6}Ni_{0.4}Fe_2O_4$ and study their inhibitors' characteristics on carbon steel using Iraqi bentonite clay as the corrosive source. Resulting data have been compared with bulk studies.

3. Nano Ferrites as Corrosion inhibitors

Recent investigations have shown that spinel based inorganic pigments have a distinctive thermal and climate degradation resistance in addition to their green environmental impact [11-16]. These materials are produced by a combination of two or more cations in the lattice structure. Their properties are largely determined through their lattice features. These types of pigments did not only enhance the mechanical strength of the binder but also decreased its permeability towards corrosive species.

Ferro-fluids also have been presented as a new material containing ferromagnetic nanoparticles as a corrosion inhibitor [4]. These magnetic fluids involve a numerous ferro-magnetic particles coated with dispersant and suspended in a carrier fluid. These magnetic particles can be magnetized and have a size range from 3 to 15 nanometers. The performance of these particles relies on the existence of a magnetic field and hence the fluid can be used for different applications including corrosion inhibition [17-19].

4. Experimental Method

All chemical materials were used as received. The synthesis of ferro-materials used for the preparation of $ZnFe_2O_4$ and $Zn_{0.6}Ni_{0.4}Fe_2O_4$ ferrite nano-composite was reported in earlier studies and described briefly later.

The base mud samples were prepared using commercial Iraqi bentonite clay supplied by (the South Oil company), containing only fresh tap water and bentonite clay. The concentration of bentonite was fixed at an optimum value of 20g with 300g of water to obtain a bentonite mass fraction of 6% and a bentonite-to-water ratio of 8%. The bentonite-to-water ratio was maintained constant for all subsequent mud samples used in this work. Other mud samples of bentonite and water with nano-ferrites additives concentrations were prepared and their effects on carbon steel corrosion were monitored. Only small concentration of additives was tried as suggested by previous studies [4,6]. A fixed small nano-

ferrite concentration of 50 ppm was added to all the samples of the Iraqi clay (bentonite) over an exposure time of 0 to 500 hrs. All corrosion measurements were done at ambient conditions of about (298K) using the corrosion rates of the coupons were monitored by weight loss technique.

The test specimens used for this work were commercially available mild carbon steel coupons obtained from the local market. These coupons were of uniform dimension ($\varnothing 25$ mm diameter and 3mm thickness). The initial weights of the coupons were taken to the nearest 0.0001 g on a digital electronic weighing balance (KERN-German made). Before use, surfaces of the specimens were polished with successively smaller grits of fine emery paper to a mirror finish, rinsed with distilled water, then degreased with acetone and dried in air at room temperature before total immersion in 100ml of the test solutions with and without the additives at different concentrations. The weight loss of each of the coupons was determined at intervals between 72 hours to 500 hours. After that, the coupon was taken from each container and washed with water, then in acetone using ultrasonic bath (SilverCrest- 46kHz, 50W) to remove the corrosion products, and finally rinsed with deionized water. The coupons were then dried and weighted to obtain the new mass. The weight loss within the immersion period was determined as the difference between the initial weight prior to immersion and final weight after immersion, and the corresponding corrosion rates were calculated. The corrosion rate calculations were carried out using standard equation. The coupons were visually examined progressively with the aim of identifying the nature of the oxide scales clinging to the surfaces of the specimens and the type of corrosion occurring.

5. Synthesis and characterization of nano-Ferrites

$ZnFe_2O_4$ and $Zn_{0.6}Ni_{0.4}Fe_2O_4$ nanoparticles have been synthesized using chemical co-precipitation process. All the materials were supplied by PETRONAS chemical lab with high purity grade. $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and NaOH were used as raw materials. Salts dissolved in de-ionized water for 30 min stirring. Sodium hydroxide (NaOH) solution was added to the salt solution. The powder-precipitated product was filtered and washed several times with de-ionized water. Then precipitated powders dried at 150 °C for

overnight. The calcination of the nanoparticles powder was done at 600 °C for 4 hrs
 The ZnFe₂O₄ and nickel doped with ZnFe₂O₄ ferrite nanoparticles samples were characterized using X-ray diffraction (XRD) in the 2θ range of 20°-80° with a scan speed of 3° min⁻¹. Figure 1 shows that all samples have a single phase cubic spinel structure (JCPDS file no. 01-074-2401) and there are no extra peaks which confirmed phase purity of the ferrite samples. The average crystallite size can be calculated by using Sherrer's formula $D = 0.9k/\beta\cos\theta_{hkl}$, where β is the full-width at half-maximum for the (311) peak, λ is the wavelength of the XRD radiation (1.5406 Å) and θ is the angle between the incident and the diffracted beams. The prominent diffraction planes (200), (220), (311), (400), (422), (511), (440) are shown by both samples. The lattice constant (a) was calculated using the equation $a = d(h^2+k^2+l^2)^{1/2}$. Crystalline size and lattice parameters are given in Table 1.

Table 1: Average grain size and saturation magnetization of the ferrite samples at 600°C.

Compositions	Average Grain size (nm)	Saturation magnetization (emu/g)
ZnFe ₂ O ₄	19.7	37.9
Zn _{0.4} Ni _{0.6} Fe ₂ O ₄	26.1	81.3

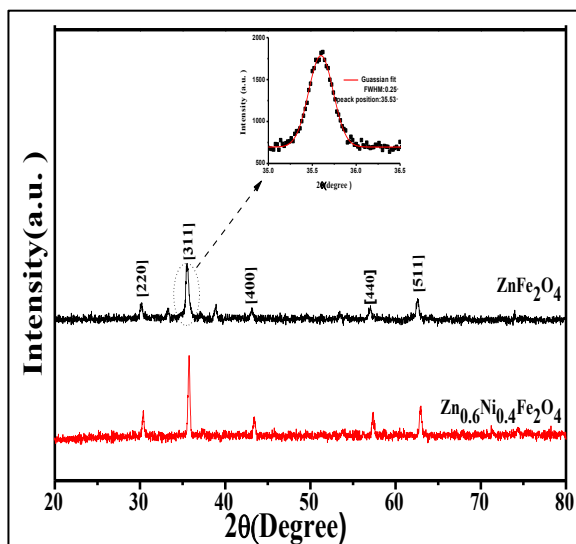


Figure 1: XRD patterns of the ZnFe₂O₄ and Zn_{0.4}Ni_{0.6}Fe₂O₄ nanoparticles.

As shown in Figure 2, the formation of ZnFe₂O₄ and Zn_{0.6}Ni_{0.4}Fe₂O₄ spinel ferrites were confirmed by Fourier Transforms Infrared Spectroscopy (FTIR) through the characteristic of two fundamental bands (ν₁ and ν₂). The first band 'ν₁' is due to the tetrahedral Fe³⁺-O²⁻ while the other one 'ν₂' related to octahedral Fe³⁺-O²⁻ complexes. According to Waldron there are two high and low frequency bands characterizing of ferrites in the

range of 200–600 cm⁻¹. The higher absorption band ν₁ is attributed to the stretching vibration mode of metal-oxygen in the tetrahedral sites, whereas ν₂ is assigned to octahedral group complexes.

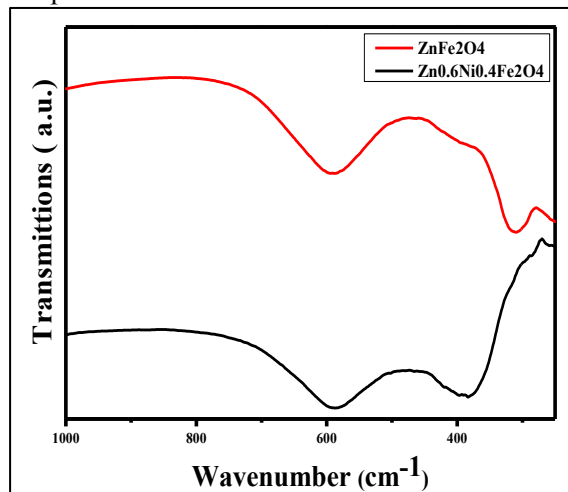
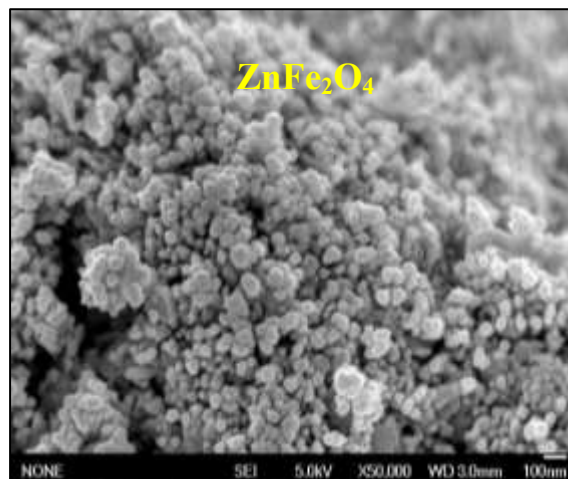


Figure 2: FT-IR spectra of the ZnFe₂O₄ and Zn_{0.4}Ni_{0.6}Fe₂O₄ systems.

SEM micrographs of ZnFe₂O₄ and Zn_{0.6}Ni_{0.4}Fe₂O₄ ferrite samples are illustrated in Figure 3. The micrographs indicated the nanostructure nature with nearly spherical shape in nanometer. FE-SEM image has shown that several nano-ferrites are agglomerated; this phenomenon is due to the magneto static interaction between magnetic nanoparticles or these nanoparticles tendency to reduce the specific superficial area that will lead to achieve lower free energy state or may be due to permanent magnetic moments proportional to nanoparticles volume.

Figure 4 shows the M–H curves for both ferrite samples. It is revealed that by the addition of nickel to zinc ferrite the saturation magnetization will be increased because of the high magnetic moments of nickel compared to zinc as a diamagnetic host material.



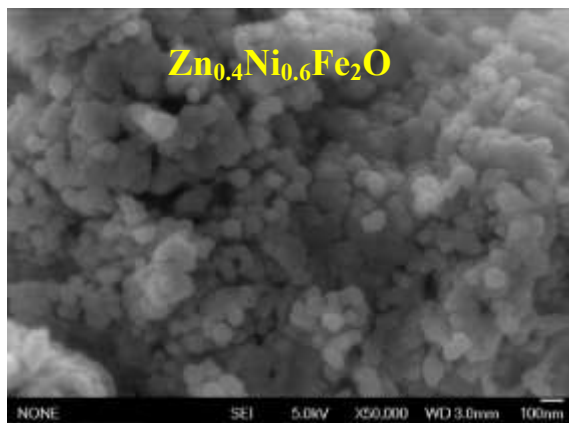


Figure 3: FE-SEM images of the $ZnFe_2O_4$ and $Zn_{0.4}Ni_{0.6}Fe_2O_4$ ferrite nanoparticles.

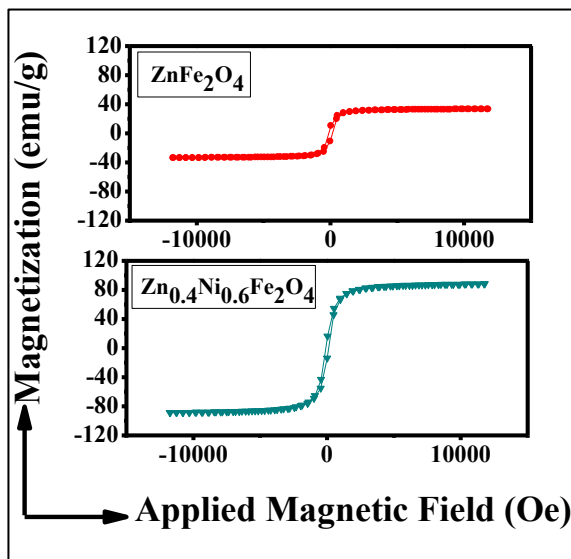


Figure 4: VSM of $ZnFe_2O_4$ and $Zn_{0.4}Ni_{0.6}Fe_2O_4$ nanoparticles at room temperature.

6. Results and Discussion

Most drilling fluid formulations contain a base liquid and additives, which must be dissolved or mechanically dispersed into the liquid to form a homogenous fluid. The resulting fluid may contain one or more of the following: water-dispersible (soluble) polymers or resins, clays or other insoluble but dispersible fine solids and soluble salts. In this work, the addition of some inorganic materials to the drilling fluid has been chosen and studied. The base liquid has been selected as the bentonite, the additives have been selected as nickel and zinc ferrites ($ZnFe_2O_4$ and $Zn_{0.4}Ni_{0.6}Fe_2O_4$), both before and after calcinations in an oven at $600^\circ C$.

The X-Ray Fluorescence (XRF) composition of the commercial bentonite is shown in Table 2. Also the X-Ray diffraction (XRD) analysis has shown that the main constituent of the commercial Iraqi bentonite is montmorillonite and Quartz. In addition, the XRD analysis of the commercial mild carbon steel is shown in Table

3. Mild carbon steel typically has a carbon range of 0.31% to 0.60%, and a manganese content ranging from 0.06% to 1.65%. This product is stronger than low carbon steel, and it is more difficult to form, weld and cut. Mild carbon steels are quite often hardened and tempered using heat treatment.

The corrosion experimental results are shown in Figures 5 and 6, which show the relation between weight loss, and corrosion rate against the exposure time respectively.

Table 2: The composition of the Iraqi bentonite clay used in this study.

Conc.	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	MgO	K ₂ O
Clay	64.97	12.59	1.03	2.75	2.49	1.12

Table 3: The composition of the mild carbon steel used in this study.

Conc.	C	Si	Mn	P	S	Fe	Rem.
Carbon Steel	0.38	0.14	0.44	0.03	0.02	98.98	0.01

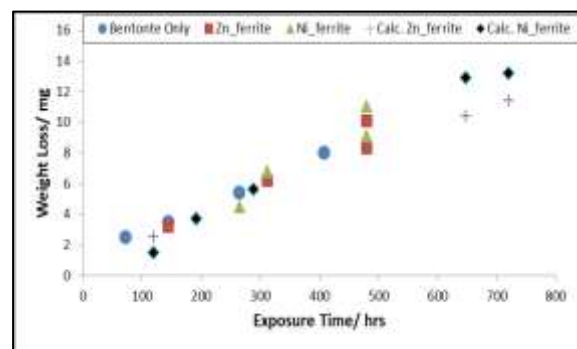


Figure 5: Weight loss against exposure time of carbon steel.

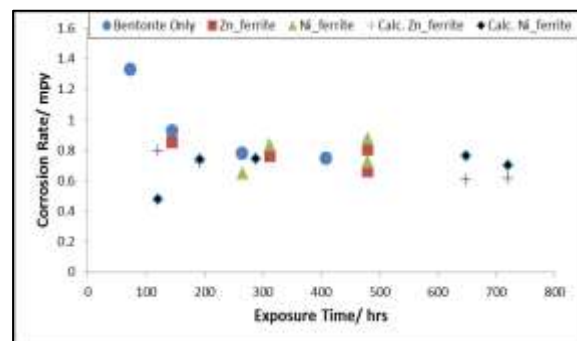


Figure 6: Corrosion rate comparison of carbon steel.

Figure 5 shows the relation between weight Loss and exposure time for the five systems. It is clear from the figure that the metal loss has been increased with exposure time. In addition, a reduction in weight loss for the ferrites and bentonite system after high temperature calcinations in comparison to the bentonite only and bentonite and ferrites before calcinations has been observed.

Figure 6 shows the relationship between the corrosion rate and exposure time for the five systems (bentonite only, bentonite/nanoZn-ferrite, bentonite/nanoNi-ferrite, bentonite/nanoZn-ferrite-calc., and bentonite/nanoNi-ferrite-calc.). The first experiments were carried out on bentonite only as the corrosive medium, which shows a corrosion rate of 0.949 ± 0.20 mpy over exposure time of 0-500 hrs. Both ferrites ($ZnFe_2O_4$ and $Zn_{0.4}Ni_{0.6}Fe_2O_4$) show the some reduction trends in corrosion before calcinations of 0.77 ± 0.2 . On the other hand, more reduction in corrosion rate was obtained after adding calcinated nano-ferrites. A corrosion rate of 0.69 ± 0.20 mpy was obtained for the nano-fluid of ferrites materials and bentonite after calcinating the ferrites materials at $600^\circ C$ overnight. Figure 7 shows the corrosion rate comparison between these systems.

Nano-ferrites can be dispersed in various polar carrier fluids such as water to arrange magnetic nano-fluid. Composition of tetrahedral and octahedral position of the ferrite modifies the properties of the fluid such as magnetic property, resistivity, thermal conductivity and electrical conductivity. Cations circulation among tetrahedral and octahedral position of ferrites reproduce the magnetic property. Magnetic moments of all the cations existing in tetrahedral site are oriented anti parallel to that of the cations of octahedral site. Therefore, the distribution of cations over these tetrahedral and octahedral locations and their exchange interaction chooses the properties of ferrites [12,17].

Ferrites zinc and nickel zinc ferrite are especially valuable due to their high electromagnetic properties, reasonable saturation magnetization and good chemical stability. Nano-ferrites are soft magnetic materials with narrow hysteresis, and thus high permeability. These materials are precipitated on the surface and delay the electrochemical reaction for the movement of ionic and non-ionic species on the metal surface [12].

The only available results to compare with are that of Kinnari Parekh et al. [20]. This work described the mechanism responsible for the inhibiting action of magnetic nano-fluid in the strong acidic media. One mechanism put forward by Kinnari et al. is that "the observed inhibitive action is due to the adsorption of magnetic nanoparticles on the steel surface, forming a barrier between the metal and the aggressive environment".

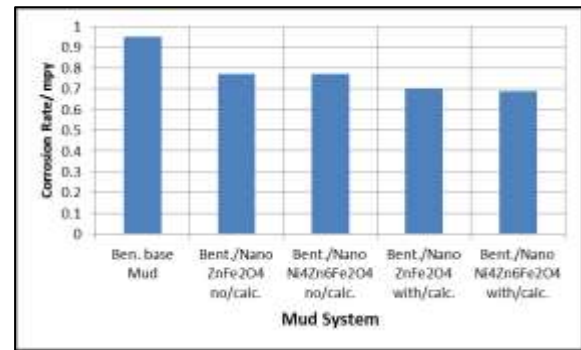


Figure 7: Corrosion rate comparison for the mud systems

7. Conclusion

There are numerous areas in which nanotechnology can contribute to more-efficient, less-expensive, and more-environmentally sound technologies than those that are readily available. Nano ferrites are important magnetic materials because of their remarkable magnetic and electrical properties and possess high chemical and thermal stabilities. These nano-particles have been used in this work to investigate their inhabitation characteristics in bentonite drilling fluids on carbon steel corrosion. Two nano-ferrite materials ($ZnFe_2O_4$, $Zn_{0.6}Ni_{0.4}Fe_2O_4$) have been synthesized and their corrosion rates were investigated and found to act as efficient corrosion inhibitors after calcinations at $600^\circ C$. A reduction of about 35% in corrosion rate was achieved when using these nano-ferrites with bentonite as a non-fluid. Further work is required to evaluate the effect of varying the concentration of the nano-material and study the effect of adding other additives such as CMC and Berite to the nano-fluid on the corrosion rate. In addition, other experiments (using Potentiostat electrochemical technique) are also necessary to validate our results

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Author(s) biography



Najem Abdulkadhim Al-Rubaiey completed his BSc in 1988 on Chemical Engineering from University of Technology, Baghdad and his MPh leading to PhD in 1995 on Physical Chemistry from Reading University, UK. He started

his job journey as a senior research in the IAEC, Iraq. He later moved on to the University of Technology, Baghdad as an assistant professor and the director of English language center for 5 years. He is currently the Labs manager and assistant professor in the Petroleum Technology Department/University of Technology, Baghdad. He has published more than 20 papers in respected journals. He also has participated in many international conferences, programs and workshops such as Fulbright visiting program in Arizona, USA, KOICA (Korea International Cooperation Agency) workshop in Seoul, South Korea and NANOP2016 conference in Paris, France.



Fadhil Sarhan Kadhim received his BSc degree in Petroleum Engineering from the University of Baghdad in 1989 and his MSc degree in 1996. He obtained his PhD in Petroleum Engineering from the UTM/ Malaysia in 2016.

Currently, Dr. Fadhil Kadhim is one of the staff members at the University of Technology, Baghdad,

Iraq. He has published more than 17 papers and one book in his specialized area. He has attended more than five international conferences.



Ali Aobid Ati completed his BSc in 2007 in the physics department, at the University of Wassit, and his MSc was in biomedical and medical physics instrumental from University of Pune-India in 2010.

His PhD program was obtained in 2015 on material science/nanotechnology from University Technology Malaysia (UTM), Malaysia. He started his job as a senior researcher in the University of PETRONAS, Malaysia. He later moved on to the University of Technology, Baghdad as a researcher in the center of nanotechnology and advanced materials. He has published more than 15 papers in local and international journals. He also has participated in many international conferences, programs and workshops.