Preparation and characterization of iron oxide modified diatomite system

Rezig W.* and Hadjel M.

Laboratory of Sciences and the Technology and Process Engineering LSTGP, Faculty of Chemistry, Department of Industrial Organic Chemistry, University of Sciences and the Technology of Oran Mohamed Boudiaf USTO-MB, Algeria

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ABSTACT

Diatomite is a rock formed primarily by frustules accumulation in diatoms called " kieselgühr " obtained from the Sig deposit located in the westward of Algeria. The diatomite, which will be modified by ferric oxide "the deposit of ferrihydrite on raw diatomite by $FeCl_2.4.H_2O$ ".The iron oxide -modified diatomite system was made through surface modification treatments including NaOH treatment an iron oxide deposition on raw diatomite.in the NaOH treatment to increase the surface area of diatomite,surface SiO_2 of diatomite was partially dissolved in the NaOH solution, .This product of this procedure was named DMF1. Comparison of XRD results proves that raw diatomite has an irregular structure but it becomes more regular at ferrihydrite modified to obtain ferric oxides differents phases from cristallinities are: ferrihydrite , maghemite, magnetite, akaganeite, hematite, goethite, and schwertmannite.The surface area of raw diatomite DB, and DMF1 were calculated as 307.8, and 231 m^2g^{-1} respectively .The point of zero charge (pH_{PZC}) which were as : 5.9 for DB, and 6 for DMF1.

Keywords: Diatomite, Iron oxide , surface charge , pH_{PZC}
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INTRODUCTION

The principal phases of ferric oxide in nature are, in order of increasing crystallinity ,ferrihydrite maghemite (γ-Fe_2O_3), lepidocrocite (γ-FeOOH), hematite (α-Fe_2O_3), and goethite (α-FeOOH) [2].The least crystalline ferrihydrite is a brown ferric oxide with a large surface area [3].Ferrihydrite is also known as a transient phase of ferric oxide [4].Irradiation, it was reported that impurities (eg., Si and P) of ferric oxide with a substantially lower content played an important role in this transformation [5].Ferrihydrite transformation in characterized by a decrease in surface area and an increase in particle size [6].Furthermore the relative low particle size of iron oxides gives way to a low hydraulic conductivity [7],which makes iron oxides solely not adaptable as a filter medium to column filtration units.To cope with this issue,granular ferric hydroxide adsorbents have been condidered.These materials are prepared by precipitating iron (III) salt under alkaline condtions followed by centrifugation and granulation under high pressure [8].An alternative to granular ferric hydroxide adsorbents consisting of iron oxide dispersed on a host matrix,which is preferably environmental friendly,cost effective and easily adaptable to column filtration process.Among these materials are diatomite ($SiO_2.nH_2O$),also known as diatomaceous earth or kieselgühr,which refer to a soft lightweight rock composed of amorphous silica microfossils of aquatic algae[9].Those skeletal remains feature a wide variety of shapes and sizes,typically between 10 and 200 µm and a particular structure consisting of macroporous channels,which pore size ranges from the submission up to tens of microns scale.As such,diatomite have attracted much attention since widely in use on a various range of applications as filtering media,catalytic support or adsorbents [10-12].Jang et al.[13] have for example successfully prepared hydrous ferric oxide incorporated into diatomite .FHMD was produced through partial dissolution of diatomite in 6M NaOH followed by hydrolysis and oxidation of 1M $FeCl_2$ [14].This compound was made through diatomite surface modification treatments including NaOH treatment and ferrihydrite deposition on raw diatomite [14]. On same

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direction, the objective of this study was to develop a simple method for preparation of iron oxide modified diatomite system which consisted mainly of crystallized hydrous ferric oxide (FeOOH) by an environmentally friendly process, Diatomite is a rock formed primarily by frustules accumulation of diatoms called "diatomite or kieselgühr" in the layer of Sig having the advantage of being locally available and less expensive. The diatomite which will be modified by ferric oxide "the deposit of iron oxide on raw diatomite by $FeCl_2.4H_2O$ " and NaOH to increase the specific surface area of this material.

MATERIALS AND METHODS

The coating Material was a raw diatomite (DB,Brand name) also called kieselgühr the sig deposit located in the westward of Algeria.It is presented in the form of a powder with white Colour.After crushing and sifting,the size of fraction particles lies between 0.4-0.6 mm.This materials is of great interest and has several uses such us : purification of drinking water.adsorbent of the pesticides, manufacture of antibiotics, some pharmaceutical syrups and its qualified like friendly material with to respect the environment [15].The choice of this material was indicated to us by the fact that : it is very abundant; it has a adsorptive affinity towards the heavy metals [16,17], and organic molecules [1,18].

Iron modified modified diatomite (DMF) preparation details have been previously reported [14] and are summarized here. Chemical composition of raw diatomite (DB) studied was determined by x-ray fluorescence (XRF) (Philips PW 1404, Eindhoven, Netherlands). DB is composed of 68.017 % SiO_2 , 19.25 % CaO, 7.575 % Al_2O_3, 2.0222 % Fe_2O_3, 1.241% MgO, 1.491 % K_2O, 0.2 % Na_2O, 0.14 % TiO_2 , 0.038 % MnO, and 0.022 % others oxides . The results are given in **Table 1**.

Table 1. Chemical Analysis of the raw diatomite

Constituents	Raw Diatomite (%)
SiO_2	68.017
CaO	19.25
Al_2O_3	7.575
Fe_2O_3	2.022
MgO	1.241
K_2O	1.491
Na_2O	0.2
TiO_2	0.144
MnO	0.038
Others oxides	0.022

DB samples (45 g) were immersed in 300 ml 6M NaOH solution at 90°C for 2h to partially dissolve Si [17].The mixture was immediately added to 300 mL $FeCl_2.4H_2O$ solution concentration (1M)and stirred and oxidized in air at room temperature (25°C) for 24 h.The mixture was centrifuged with at a of rate 12000 rpm for assorted the separation .The solid obtained through centrifugation was washed with distilled water and oxidized in air at room temperature overnight.The mixture was centrifuged for 30 min with rate 15000 rpm for assorted the separation to remove the excess of NaOH.The solid obtained through centrifugation was washed with distilled water and oxidized in air to continue the oxidation $Fe(OH)_2$ and remove the excess of NaOH for 24h.The mixture was dried at 105°C for 24 h. This Product of this procedure was named DMF1.

Chemical composition of iron oxide modified diatomite (DMF1) studied was determined by x-ray fluorescence (XRF) (Philips PW 1404, Eindhoven, Netherlands). DMF1 is composed of   35.335 % SiO_2 , 21.138 % Na_2O, 19.857 % Na_2O , 19.857 % , 17.865 % , 3.094 % CaO, 1.718 % Al_2O_3 , 0.644 % MgO , 0.349 % K_2O. The results are given in **Table 2.**

Table 2. Chemical Analysis of DMF1

Constituents	DMF1 (%)
SiO_2	35.335
Na_2O	21.138
Cl_2O	19.857
Fe_2O_3	17.865
CaO	3.094
Al_2O_3	1.718
MgO	0.644
K_2O	0.349

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The surface area of DMF1, was determined, according to Sears method [19],by weighing 0.5 g of DMF2X6, and acidifying with dilute hydrochloric acid to pH of 3-3.5.Sodium chloride (10g) was then added with stirring,and the mixture was made up to a total volume of 50 ml with distilled water.The solution was titrated with 0.1M sodium hydroxide NaCl and the pH measured throughout the titration process.The volume,V, required to increase the pH from 4 to 9 was recorded.The surface area (S) was estimated from the equation (1) [17] :

$$S \ (m^2 g^{-1}) = 32\ V - 25 \qquad (1)$$

Where 32 and 25 are Sears empiric constants.The surface charge of calcined ferrihydrite modified diatomite "DMF2X6" was determined by a potentiometric titration method (Chen et al.,1996; Chen and Lin,2001)[20,21].The same concentration of the DMF2X6, used in this manipulations are $1 gL^{-1}$ were first placed in the shaker for 2h at room temperature.Titrations were then carried out by using 0.1 M hydrocholoride acid and then 0.1 M sodium hydroxide,and the pH was measured throughout the titration process.The volume (ml) of acid or base needed to change the pH from 3 to 12 was recorded, duplicate samples were measured ant he results were reported as an average.

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RESULTS AND DISCUSSION

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The mineralogy of DMF1 was characterized by powder x-ray diffraction (XRD) analysis using a model Bruker Axe Gmbh, D8 Advance Cu Kα radiation (λ = 0.1540598 nm , 50 kV, 100 mA). The powder sample was coated on a plate out of glass of methanol and were dried with the room temperature, then swept $1°$ with 80° (2Θ) with the size of stage of 0.020°.Results are shown in **Fig.1**.

For the DMF1 : for the quartz : (the peaks at 2Θ = 26.4°-45.5°-56.5°-66°) [65,66],for the calcite (the peak at 2Θ = 45.5°) [65,66],for the lepidocrocite (the peak at 2Θ = 26.4°) (ASTM file N° 8-98),for the kaolinite (the peak at 2Θ = 26.4-41.2°-45.5°-53.5-56.5°) (ASTM file N°14-164) [67],for the Opal-A (the peak at 2Θ = 26.4°), for the akaganeite (the peak at 2Θ = 26.4-35.5°) [44] ,for the illite (the peaks at 2Θ = 26.4-35.5-41.2°-45.5°) (ASTM file N° 9-343) [67],for the rutile : (the peak at 2Θ = 27.5-53.5°) (ASTM N°4 – 551),for the ferrihydrite : (the peak at 2Θ = 27.5°-35.5°-45.5°-53.5°) [68],for the hematite (the peak at 2Θ = 35.5°-53.5°-56.5°) [44],for the anatase (the peak at 2Θ = 53.5°) (ASTM file N°4-447) [67], for the magnetite : (the peak at 2Θ = 35.5°) [44], for the magnetite : (the peak at 2Θ = 35.5°) [44], for the ferroxide (the peak at 2Θ = 35.5-53.5°) [44], for the enstatite : the peak at 2Θ = 35.5°) (ASTM N° 7-216), for the schwertmannite : (the peak at 2Θ = 35.5°) [44], for the ilmenite : the peak at 2Θ = 35.5° (ASTM file N° 3-781), for the sodium chloride (the peaks at 2Θ = 27.5°- 45.5°- 53.5°- 56.5°- 66°) (JCPDS pdf N° 5-628) [68].
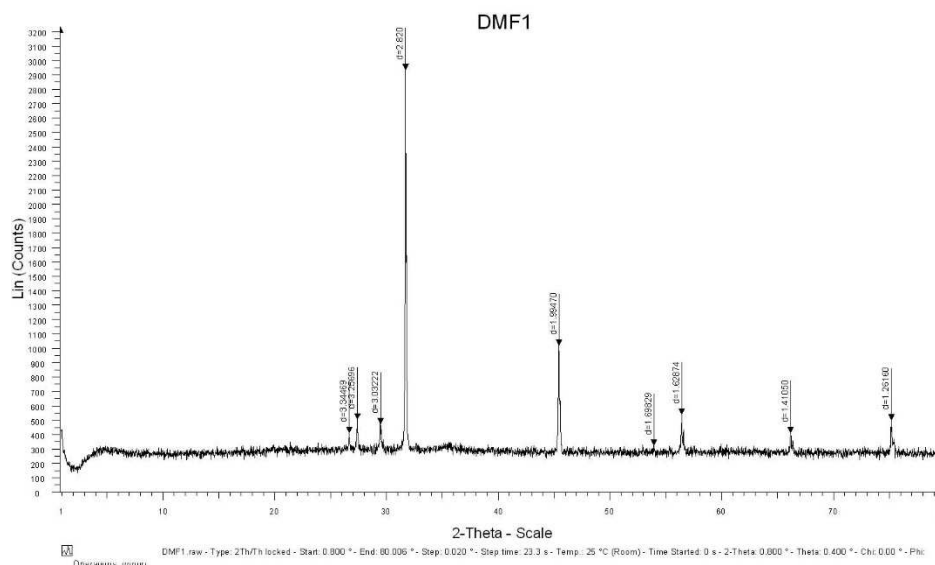

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Fig. 1. X-ray diffraction pattern of DMF1

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FTIR spectra of ferrihydrite modified diatomite (DMF1) with help of spectrometer using a model Bruker α Alpha H Gmbh D8 FTIR between 4000 cm^{-1} and 400 cm^{-1}, and a resolution of 4 cm^{-1}; 28 scans were performed . the sample is conditioned with the dispersion form in the powder of DMF1X . The result is shown in **Fig.2**.

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For the DMF1, the absorption band at 3352.33 cm^{-1} refers to monomeric hydrogen bonds,which are assigned in diatomite system to Fe-OH species present on surface,indected in the case of non-hydroxylated atoms. The surface irons atoms tend to complete their coordination shell by reacting with water molecular in order to form surface Fe-OH species [72],furthermore the observed shift indicates on the one hand some noticeable changes caused to frustule surface H-bonded silanols (previously identified by vibration mode at 3399.89 cm^{-1},[69] during DMF1 system formation and on the other hand the increase of hydrogen bonding in DMF1 system [73,74].The absorption band at 2320.93 cm^{-1} corresponds the vibration of Si-H [75].

The absorption band at 1635.41 cm^{-1} corresponds the vibration of $Fe(OH)_3$ [76]. The absorption band at 1455.18 cm^{-1} corresponds the vibration of $CaCO_3$,and $CaFe(CO_3)_2$ [77],and $FeCO_3$ [78].The absorption band at 992.88 cm^{-1} is attributed to asymmetric Si-O stretching vibration of bridging siloxane groups (Si-O-Si),which refers silicate materials that compose diatomite frustules as well as quartz phase entering diatomite composition[70], ferroxyde [44],schwertmannite [44],akaganeite (β-FeOOH [44], lepidocrocite (γ-FeOOH) [44], $Fe(OH)_2$ [44]. maghemite (γ-Fe_2O_3) [77], and ferroxhyte (δ-FeOOH) [90].The absorption band at 791.98 cm^{-1} corresponds   goethite(α-FeOOH)[44],ferroxyde[77],lepidocrocite [77], akaganeite (β-FeOOH)[44], ferroxhyte [79], maghemite (γ-Fe_2O_3)[44], hematite (α-Fe_2O_3) [77].The absorption band at 713.51 cm^{-1} corresponds the vibration of carbonates (CO_3^-)[81], lepidocrocite (γ-FeOOH) [77], akaganeite (β-FeOOH) [44], ferroxyde [44], ferroxhyte (δ-FeOOH) [79],schwertmannite[44],   and, ferrihydrite($Fe_5HO_8.4H_2O$)[90],   maghemit(γ-Fe_2O_3)[75],   hematite(α-Fe_2O_3)[44], magnetite(Fe_2O_3)[75], goethite (α-FeOOH)[44].The absorption band at 639.40 cm^{-1} corresponds the maghemite (γ-Fe_2O_3) [77],akaganeite (β-FeOOH) [44], ferroxyde [44], schwertmannite [44], ferroxhyte (δ-FeOOH) [79].The absorption band at 561.91 cm^{-1},526 cm^{-1},and,510.17 cm^{-1} correspond the schwertmannite [44], goethite(α-

FeOOH)[76], maghemite (γ-Fe_2O_3) [44], magnetite (Fe_3O_4),[44], hematite (α-Fe_2O_3) [44].The absorption band at 452 cm^{-1}   corresponds   the-hematite(α-Fe_2O_3)[44],maghemite(γ-Fe_2O_3)[44],magnetite(Fe_3O_4)[44],akaganeite(β-FeOOH) [44], schwertmannite[44], The absorption band at 400.92 cm^{-1} corresponds the hematite(α-Fe_2O_3) [44],maghemite (γ-Fe_2O_3)[44],magnetite   (Fe_3O_4)[44],akaganeite (β-FeOOH) [44].
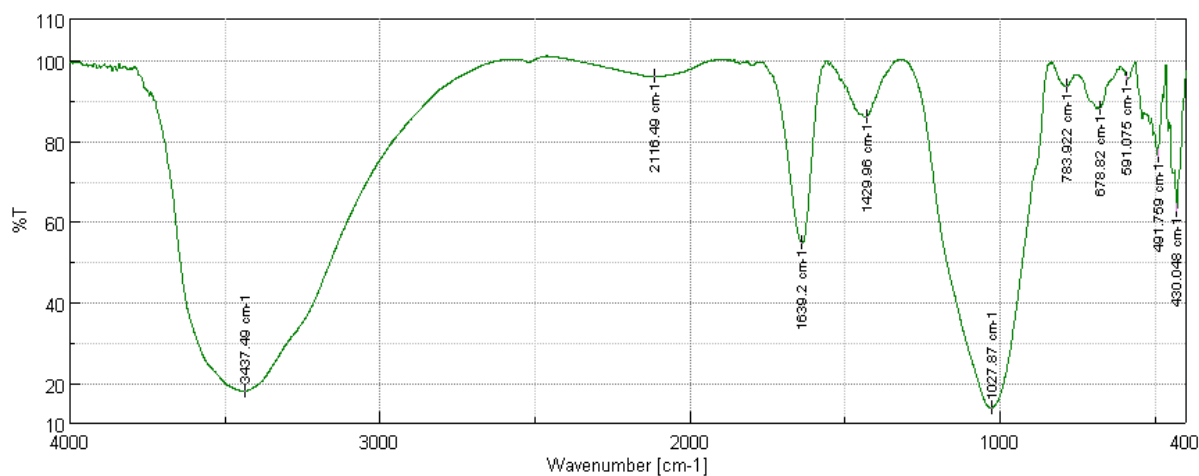

Fig. 2. FTIR spectra of DMF1

The morphologies of the mineral phases constituting the samples were investigated by scanning electron microscopy using a model (JEOL JSM 6610 La , Japan) scanning electron microscopy .The sample was first mounted flat,using carbon tape, and then coated with 30 nm of gold using a sputter coater, the working distance was set to 17 mm and then accelerating voltages of 20 keV were used.

Fig.3. shows an electronic micrograph of micrograph of iron oxide modified diatomite (DMF1).There are two principal types of pattern in DMF1 particles have a diameter of approximately 3-6 μm and a thickness of several microns.The pennate of DMF1 particles have a length of approximately 4-9 μm.
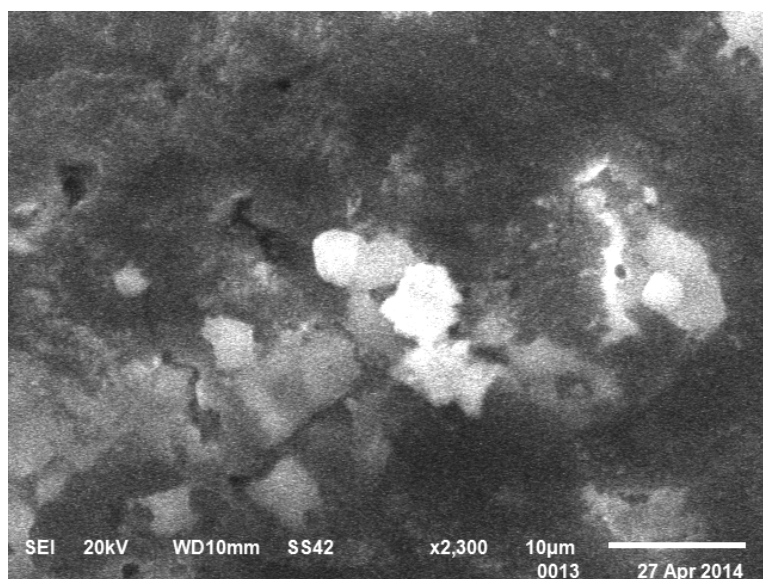
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Fig. 3. Scanning electron micrograph of DMF1 (magnification 2300 X)

The surface area of DMF1 used in this study was calculated by Sears method [61] as 231 m^2/g.

The surface charge density (C/m^2) is determined by the following [80] :

$$\sigma = (C_A - C_B + [OH^-] - [H^+])\, F/\, Am \qquad\qquad (1) \qquad [80]$$

Where C_A and C_B are the concentration of acid and base needed to reach a point on the titration curve, in mol/L, $[H^+]$ and $[OH^-]$ are the concentrations of H^+ and OH^- converted from pH , in mol/L, F is the Faraday constant (96490 C/mol), A is the specific surface area, in m^2/g , and m is the concentration of DMF1, in g/L.

The surface charge of DMF1 as function of solution pH is shown in **Fig.4**.
The titration curve illustrates that the surface charge decreases as the pH is increased .The intersection of two curves with x-axis gives the point of zero charge (pH_{PZC}) which was 6 for DMF1. In this study, at pH_{PZC} , the total charge from cations and anions at the sample surface is equal to zero. The surface charge is negative when the solution pH is above pH_{PZC} and becomes positive when pH below pH_{PZC}.
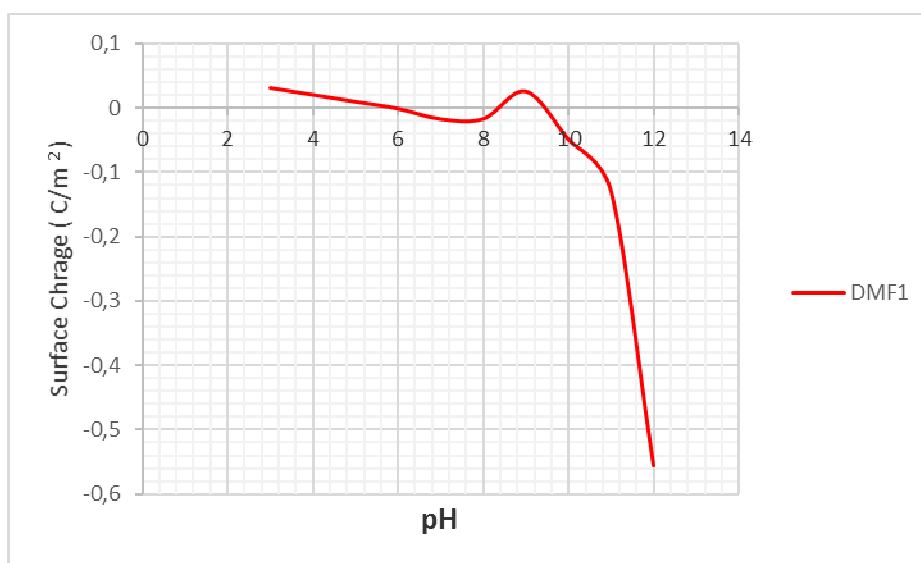

Fig. 4. Surface charge density curve of DMF1

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CONCLUSION

The characterization of raw diatomite DB by various analytical techniques showed that natural diatomite is composed mainly of amorphous silica (68.017 %),with $CaCO_3,Al_2O_3$ as the main impurities of the order 19 %, and 7% sequentially from x-ray fluorescence (XRF).Iron oxide modified diatomaceous earth has been synthesized by precipitating iron oxyhydroxide phases onto the surface of the silica skeleton of the biomeneral. The modification of diatomite has been conducted is one pot consisting of the precipitation of ferrous ions (Fe^{2+}) by the hydroxyls generated by the dissolution of CaO present in diatomite composition. The results of fourier transform infrared (FTIR), and x-ray diffraction (XRD) show that the ferrihydrite–modified diatomite (DMF1) different phases of ferric oxide are : ferrihydrite, maghemite, lepidocrocite, hematite,goethite,schwertmannite,ferroxhyte, akaganeite,ferroxyde,and magnetite.The scanning electron microscopy (SEM) from DMF1,there are two principal types of pattern in DMF1.The centric of DMF1 particles have a diameter of approximately 3-6 μm and a thickness of several microns,and the pennate DMF1 particles have a length of approximately 4-9 μm.The surface area of ferrihydrite- modified diatomite (DMF1) was calculated as 195.8 m^2g^{-1} .The pH of point of zero charge (pH_{PZC}) which was as 6 for DMF1. As concluded about the iron oxide modified diatomite (DMF1) by the formation of new structure through bonding Si-O-Fe .

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