Computational study of the interaction between azo dye (RR141) and Hematite α-Fe2O3 (111) Surface: A DFT and MDs Study

M. E. Belghiti
Hassan II University of Casablanca

K. Mizeb
Ibn Tofail University

M. Salah
Chouaïb Doukkali University

A. Zeroual
Chouaïb Doukkali University

J. Mouldar
University Chouaib Doukkali

A. Moubarik
Sultan Moulay Slimane University

M. Hochlaf
University of Gustave Eiffel, COSYS/LISIS

M. El idrissi (✉ m.elidrissi2018@gmail.com)
Sultan Moulay Slimane University

Research Article

Keywords: Adsorption, Reactive-Red 141 dye, Mineral Hematite, DFT, Molecular Dynamic simulations

Posted Date: January 6th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2428353/v1

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Computational study of the interaction between azo dye (RR141) and Hematite α-Fe₂O₃(111) Surface: A DFT and MDs Study


1Laboratory of Chemistry-Physics of Materials, Faculty of Sciences, Ben M’Sick, Hassan II University of Casablanca, Casablanca, Morocco.
2Laboratory of Nerness Technology, 163 Willington Street, Sherbrook, J1H5C7, Quebec, Canada.
3Laboratory of organic chemistry, inorganic, Electrochemistry and Environment, Department of Chemistry, Faculty of Sciences, Ibn Tofail University, Kenitra, Morocco
4Molecular Modeling and Spectroscopy Research Team, F. Sc, Chouaib Doukkali University, El Jadida, Morocco.
5Laboratory of Organic Chemistry, Bioorganic and Environment, F. Sc, University Chouaib Doukkali, El Jadida, Morocco
6Team of Chemical Processes and Applied Materials, Faculty Polydisciplinary, Sultan Moulay Slimane University, Beni-Mellal, Morocco.
7University of Gustave Eiffel, COSYS/LISIS, 5 Bd Descartes, 77454 Champs sur Marne, France
* Corresponding author: E-mail: m.elidrissi2018@gmail.com

Abstract

The adsorptive removal of azo dye molecules from textile effluents by the powdered mineral hematite has been largely studied in the literature, but this mechanism of interaction with the mineral hematite surface is still to date not revealed, hence the need for a theoretical study. The crystal structure model of Hematite adopted is $\alpha-\text{Fe}_2\text{O}_3(111)$. The DFT method and MDs(Molecular Dynamics simulations) have been employed to elucidate the mechanism of interaction. The azo-dye molecule chosen for this study is the reactive red RR141. Geometry minimization of RR141 was performed at the DFT / B3LYP / 6-31+ +g(d,p) level of theory. The reactivity and performance of RR141-vacuum and RR141-aqueous media in isolated state were evaluated on basis of their planarity, global and local electronic properties as well as deformation ability to adhesion to the mineral surface. The Azo (>N=O<) and hydroxyl (-O--H) groups are the main active centers for the adsorption of RR141 in a vacuum and aqueous media. Azo and hydroxyl groups of RR141 dye are electron donors, while the sulphonic acid (-SO$_3$--Na$^+$) group is an electron acceptor. The RR141 is found more reactive in the vacuum than in an aqueous medium. The interfacial interaction is the combined effect of the hydrogen bond and the interactions between Fe & --O--, C, --S--, N-- atoms. The whole system is interacting on the first layer through ($\pi$-$\pi$)-bonds in the nearly parallel adsorption geometries and through the single pair electrons of the heteroatoms.
Keywords: Adsorption; Reactive-Red 141 dye; Mineral Hematite; DFT; Molecular Dynamic simulations.

1. Introduction

Synthetic colorants are largely used in the textile dyeing industry [1-4], among them the Azo dyes molecules family. These molecules are highly toxic, non-biodegradable, and have carcinogenic effects on living beings [5-7]. Coagulation and flocculation technics have failed to treat this type of dye. Adsorption on mineral surfaces has been turned into the most effective method to remove dye pollutants from contaminated water[8]. The family of heterocyclic azo dyes pollutants is characterized by an azo group \((R-N=N-R')\)[9117]. The most common types of azo dyes can be summarized as follows: aryl\(-N=N-R\), where R may be aryl, heteroaryl, or \(-CH=C(OH)-\)alkyl. The azo\(-N=N-\) group plays an important role in the chemical properties of compounds containing such a functional group. The level of interaction of organic compounds is often affected by the nature of substitution which facilitates the adsorption onto mineral surfaces. The reactivity of adsorption sites of organic pollutants on regular surfaces of the mineral is enhanced by the existence of the hetero-atoms (-S-, =N-, -O-…). Thus, the presence of heteroatoms in the molecule skeleton might make the adsorption of these molecules on surfaces easier. Furthermore, in the corrosion field, the molecules with heteroatoms can be efficient corrosion inhibitors. The efficacity of these molecules has been proved experimentally and by theoretical calculations (DFT, MDs approaches) [12-14]. Mineral surfaces have attracted much attention from scientists because they exhibit properties suitable for many applications in material science and environmental engineering, they present great utility in a wide range of important fields, such as magnetization, electrochemistry, and environmental applications. Among several de-pollution technics, adsorption onto mineral surfaces is one of the effective methods to remove dyes from wastewater. Various adsorbents have been used for this kind of task, we can cite a partial list of them: Hematite, Perlite, Bentonite, Fly-ash, Diatomite, Activated Sludge, Lignite, and Silica. Iron oxides are the most abundant mineral clays in soils composed mainly of iron and oxygen elements, which can an effective material with a low economic cost for the elimination of azo dyes from textile wastewater. Indeed, most studies to date have been carried out on mineral adsorbents surfaces in which the mechanism of interaction is not evocated, making it difficult to explore the surface phenomena that prevail during the interaction between the mineral surfaces and adsorbates, hence the need for a theoretical study. Thus, the main goal of the present paper is the investigation of the mechanism of interaction on the mineral surface of hematite \(\alpha-\text{Fe}_2\text{O}_3\) (111) with an azo dye molecule (RR141). The reasons for the choice of hematite and RR141 in this study are related to the low cost of hematite material, and when it loses its surface activity, it can be discarded in blast furnaces as feed material for pig-iron production without causing environmental impact, which will encourage industrial in textile to use it. Concerning RR141 dye, it was chosen as a model azo-dye due to its common use in the textile industry, its high resistance to degradation, and its relevance as a type of compound typical of those found in difficult-to-treat effluents of textile industries. Thus, we have realized a theoretical model of Hematite \(\alpha-\text{Fe}_2\text{O}_3\) (111) in order to study its interaction with RR141 (Fig. 1), using the DFT method and Molecular Dynamics simulations.
DFT method and MDs are powerful tools to study the interaction of organic compounds on to the regular surface of minerals, elucidating the main sites of interactions[4]. This theoretical work will be very helpful to reveal the surface phenomena during the interaction of mineral surface ($\alpha$-Fe$_2$O$_3$(111)) with the RR141 azo dye, which can later be used to test theories results for sorption of azo dyes in the Hematite material.

DFT and MDs have been used to reveal the mechanism of adsorption of the precedent organic compound onto regular Hematite $\alpha$–Fe$_2$O$_3$ (111) surface, in a vacuum and aqueous media, and the type of dominant interactions in the complex RR141/mineral surface.

2. Computational details
2.1 Global quantum reactivity descriptors (GQRDs)

The interaction of the RR141 dye onto the mineral $\alpha$–Fe$_2$O$_3$ (111) surface was investigated using DFT with Gaussian 16 software package. The DFT/B3LYP/6–31+g(d,p) basis set was used because it provides accurate electronic properties and geometries for a large number of organic compounds[15-18]. The stationary points were characterized by frequency (no imaginary frequency) calculations to ensure that they are real minima[19]. The information for the chemical reactivity and the global active sites were obtained to determine the preferable sites of adsorption for organic compounds on mineral surfaces. The frontier (HOMO/LUMO) orbitals of RR141 have been used to determine its GQRDs [20-21]. A good correlation has been found between adsorption capacity and $E_{\text{HOMO}}$ associated with the electron-donating ability[22]. The adsorption of organic molecules on the mineral layer surface can occur based on donor-acceptor interactions between the $\pi$-electrons of the organic compound and the vacant 3d-orbital of the metal atoms. The high value of $E_{\text{HOMO}}$ of the adsorbate shows its tendency to transfer electrons to appropriate acceptor sites of the mineral surface, while the lower value of $E_{\text{LUMO}}$ indicates the capacity to accept electrons. The global indices (GIs) as ionization potential IP = -$E_{\text{HOMO}}$, electron affinity AE=-$E_{\text{LUMO}}$, ionization potential IP=-$E_{\text{HOMO}}$, electron affinity AE=$E_{\text{LUMO}}$, global hardness $\eta$=IP-AE/2, electronegativity $\chi$=(IP+AE)/2, electronic chemical potential $\mu$=-(IP+AE)/2, electrophilicity $\omega$=\mu$^2/2$\eta$, chemical softness $S$=1/\eta will be useful to rationalize the most favored sites of interactions which intervene during the adsorption operation[23-24]. Another method to analyze the process of adsorption is to calculate the fraction of electrons transferred between organic adsorbate and the mineral surface. The electron fraction transferred is calculated as follows $\Delta N = -(\chi_{\text{Fe}} - \chi_{\text{molecule}})/2(\eta_{\text{Fe}} - \eta_{\text{molecule}})$.

For donation and back donation of charges, there are two different parameters, $\Delta N^+$ and $\Delta N^-$, indeed the $\Delta N^+$ will be used when an organic molecule receives a certain amount of charge, while $\Delta N^-$ will be used in the case of a molecule that back-donates a certain amount of charge [25]. Consequently, the amount of energy transferred will be as follow, $\Delta E^+ = \mu^+ \Delta N^+ + \eta (\Delta N^+)^2$, and $\Delta E^- = \mu^- \Delta N^- + \eta (\Delta N^-)^2$. The variation of total energy will be as $\Delta E_T = \Delta E_{\text{back-donation}} = \Delta E^+ + \Delta E^-$. The $\Delta E_{\text{back-donation}}$ becomes a minimum regarding $\Delta N^+$, which implies that its expression will be as $\Delta E_{\text{back-donation}} = ...$.
1/8(E_{\text{HOMO}}-E_{\text{LUMO}}). For the determination of the more favorable sites of interaction between an organic compound and a mineral surface, the Fukui functions (FF) are very useful [26-27]. This FF are expressed as follows, \( f_k = (\partial \rho(r)/\partial N)(v(r) \) with N the number of electrons, and V(r) represents an external potential. The Fukui functions for nucleophilic and electrophilic attacks of the organic adsorbate have been determined as follows. \( f_k^+ = q_k(N+1) - q_k(N) \) for nucleophilic attack and \( f_k^- = q_k(N) - q_k(N-1) \) for electrophilic attack. The \( q_k (N+1), q_k (N), \) and \( q_k (N-1) \) are the charge of the anionic, neutral and cationic.

### 2.2 Molecular dynamics (MDs) simulation

MDs are becoming a powerful technique to study molecular structure and properties of organic-inorganic clay interface [28-30]. The Forcite and CASTEP calculation modules implemented in Biovia Materials Studio (formerly Accelrys) software[31], were used to evaluate the nature of the interaction between the adsorbate (organic pollutant azo dye- Reactive Red 141) and the substrate (Iron-oxide mineral surface). The RR141 is a large anionic macromolecule (\( L_x = 17.2 \text{ Å} \times L_y = 26.8 \text{ Å} \times L_z = 16.6 \text{ Å} \)) with ramifications, high molecular weight (\( M=1774.15 \text{ g/mol} \)), and high molecular volume (\( V=1117.85 \text{ Å}^3 \)). The CASTEP module was employed to minimize the geometry of iron oxide mineral surfaces [32]. The geometry minimization of hematite bulk was realized under the condition of 340 eV cutoff energy and Brillouin zone k-point of \( 2\times2\times1 \). The wave functions were converged at the limit of 2.0 eV/atom and the geometry was minimized until the forces on all the atoms were less than 0.05 eV/Å. As a consequence, the intermolecular interactions between adsorbed molecule and surface were necessary to consider ideal and real situations. The structure of bulk Hematite \( \alpha\text{-Fe}_2\text{O}_3(111) \) was modeled by a hexagonal cell consisting of six formula units and the different surface structures were modeled with \( (8\times8) \) supercells ensuring that the minimum distance between the organic RR141 pollutant molecule and its images in the neighboring cells is \( \sim 7 \text{ Å} \). The Hematite \( \alpha\text{-Fe}_2\text{O}_3(111) \) was fabricated with periodic slab surfaces that consist of four atomic layers and a vacuum slab having a thickness of \( 50\text{ Å} \) was made above the \( \text{Fe}_2\text{O}_3(111) \). The crystal (111) face of iron oxides-surface is chosen because it is among the most thermodynamically stable in the literature [33-35]. The COMPASS force field(CFF) was used for the geometry minimization of structures. The surface stabilities for different termination are determined by their surface energy, calculated using the next equation, \( E_{\text{surface}}= (1/2A) \{E_{\text{slab}}-(n_{\text{slab}})(E_{\text{bulk}})\} \), where \( E_{\text{slab}} \) is the total energy of the cell containing the surface slab, \( n_{\text{slab}} \) is the number of atoms in the slab, \( E_{\text{bulk}} \) is the total energy per atom of the bulk and \( A \) is the surface area. The interaction or binding energies of each molecule with the Hematite \( \text{Fe}_2\text{O}_3 \) (111) surface is calculated by the next formula, \( \Delta E_{\text{int}} = E_{\text{complex}} - E_{\text{substrate}} - E_{\text{adsorbate}} \), where \( E_{\text{complex}} \) is the total energy for (adsorbate/substrate) system, \( E_{\text{substrate}} \) is the energy of the iron oxides-surface before the molecule adsorption, and \( E_{\text{adsorbate}} \) is associated with the isolated organic molecule [36].
3. Results and discussion

3.1 Geometry parameters

The geometry minimization of the RR141 molecule \((C_{52}H_{26}O_{26}S_8Cl_2N_{14}N_6)\), molecular weight: 1774.15 g/mol) has been performed at the B3LYP/6-31 + +g(d,p) level of theory in vacuum (V) and aqueous phase (A) (Fig. 1S). The different geometrical parameters related to the RR141 molecule in vacuum and water with X-ray data are presented in Table 1S. The results concerning the torsion angle C_{65}-N_{71}=N_{87}-C_{72}, the length bond N_{71}=N_{87}, and bond angle C_{17}-C_{18}-O_{111} are respectively in vacuum (-174.75°, 1.237 Å, and 124.23°), as those of X-RD are (174.75°, 1.254 Å, and 120.24°), so the geometrical results of optimization are very close with X-RD data, which confirms the accuracy of our geometry optimization. In the water phase, the geometry of the organic molecule is very slightly affected (Table 1S), thus the addition of water does not affect the geometry of the molecule.

3.2 Global reactivity

The employed DFT method is suitable for rationalizing the (HOMO/LUMO). The analysis of HOMO/LUMO and related GQRDs provided valuable information to determine the RR141-global reactivity indices. The RR141-E_{HOMO} and RR-141E_{LUMO} values reflected the different electron-donating abilities and hence the different adsorption ability of organic compounds on the mineral iron oxide surface, so the LUMO molecular orbital indicates the regions of the molecule with a high tendency to accept electrons from nucleophilic centers (electron-pair donor) while the HOMO molecular orbital predicts the regions of the molecule that tend to donate electrons. Fig. 2S presents a plot of RR141-HOMO and RR141-LUMO.

The RR141-LUMO is strongly delocalized on some carbon atoms (C_3, C_6, C_9, C_16, C_{17}, C_{18}, C_{19}, C_{22}, C_{23}, C_{27}, C_{31}, C_{72}, C_{73}, C_{65}, and C_{96}) with a very significant electron acceptor effect for nitrogen atoms (N_{87}, N_{71}) and oxygen (O_{87}), while RR141-HOMO is located around the azo (=N–N=) and –N=C– moiety, oxygen atoms (O_{78} and O_{111}), nitrogen (=N30-) and some other carbon atoms (C_3, C_6, C_9, C_{12}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{22}, C_{56}, C_{58}, C_{64}, C_{67}, C_{68}, and C_{73}), this is due to the presence of the hetero (=N-&-O-) atoms together with several electrons on the entire molecule (carbon-nitrogen, carbon-oxygen, and carbon-carbon, the double bond of azine [R-N=N-R], on one hand, the group of sulphonic acid (R-SO_3^–..Na^+) was not the main functional group for the adsorption mechanism in neutral form. The anionic (RR141) molecule can accept electrons from the unoccupied 3d-orbitals of the (Fe^{2+} or Fe^{3+}) atom within its anti-bonding orbitals to form back-donating bonds (Coordinated covalent bonds) [37]. The qualitative descriptions of electronic density associated with the RR141-(HOMO /LUMO) and Density of states (DOS) plots are depicted in Fig. 2. It clearly shows an electron density distribution in molecular orbitals that suggests possible interactions, and thus almost parallel adsorption of the organic molecule pollutant onto the surface of the mineral iron-oxide [38]. The study of HOMO/LUMO anionic macromolecules provides reliable and quantitative
data for prediction and comparative study of the stability of the organic molecule from a chemical and thermodynamic point of view.

The calculation of global indices of the minimized geometry of the RR141 molecule at B3LYP/6-31++g(d,p) level of theory (Table 1) shows that the anionic macromolecule (RR-141) has the highest value of $E_{\text{HOMO}}$ in the vacuum and in aqueous media, which implies the highest tendency to donate electrons to the iron-mineral surface which will facilitate its adsorption onto the iron oxide surface.

The energy gap $\Delta E_g$ is an important stability index, this value indicates the relative stability of the RR141. A large value of $\Delta E_g$ implied lower stability. In our case, the value of the energy gap in water is 1.198 eV less than 1.386 eV in a vacuum, which means that the stability of RR141 decrease in the aqueous phase. The solvation effect on the reactivity of RR141 is to increase values relative to $\mu$ and $\eta$, and to decrease $S$ and theoretical quantity of charge transfer $\Delta N$, consequently the water weakens the ability to give electrons to the mineral surfaces. We observe an increase of DM value in water (1.438 Debye in vacuum and 2.346 Debye with water), consequently, the organic molecule becomes more favorable to interact with the surface by electrostatic forces.

3.3 Molecular electrostatic potential surfaces (MEPs)

The molecular electrostatic potential surface (MEPs) [39-41] is a useful tool for describing the electrostatic nature of the different areas of the molecule. We have realized here the MEPs of the RR141 molecule to determine the electrostatic nature of each site of the organic molecule and determine the more favored centers of interaction (Fig. 3). The Azo (N$_{87}$-N$_{71}$, N$_{16}$-N$_{30}$), hydroxy (-OH) and ionic sulphonic acid (-SO$_3^-$) groups of the reactive dye are the most electron donators (red colored) sites. These sites are the most suitable to interact with a minerale surface that needs a donation of electrons, while the blue-colored sites represent a strongly positive region (electrophillic region) located in the triazine rings.

3.4 Active sites analysis of the neutral forms of RR141

Usually, the organic molecules adsorbate on the minerale surface through a donor-acceptor (D-A) type of interaction, so it's more judicious to consider each individual atom of the organic molecule by Fukui indices (analysis, which leads to predicting the electrophilic and nucleophilic sites of the organic molecule). The values of $f_k^+$ and $f_k^-$ are presented in table 2S. Analysis results of Fukui indices indicate that N atoms are the most negatively charged, so they will be the more favored for interactions with minerale surfaces, precisely N16 ($f_k^- = -2.26$) and N71 ($f_k^- = -2.26$) atoms.

4. Molecular dynamics (MD) simulations

4.1 Reactive red (RR141) / Hematite $\alpha$-Fe$_2$O$_3$(111) interaction studies

The adsorption performance of a single organic molecule RR141 on the Hematite $\alpha$-Fe$_2$O$_3$(111) surface is dependent on the interactions between them, so we have realized a model of $\{141\text{RR}/\alpha$-Fe$_2$O$_3(111)\}$ in presence of H$^+$ and Cl$^-$ ions in order to study more completely the adsorption process. This allows us to interpret and explain the mechanism of adsorption and reveals the type
of interactions between the organic molecule and the surface by molecular dynamics simulation. The most stable adsorption geometries of RR141 dye on the Hematite α-Fe₂O₃(111) surface in acidic conditions (Fig. 4) are also given here. As seen, the RR141 molecule adopts a parallel configuration over the mineral surface α-Fe₂O₃(111). It was found that the interfacial interaction is the combined effect of the hydrogen bonds and the interactions between Fe and -O-, C, -S- & =N- atoms. The main driving force for the adsorption for {141RR/α-Fe₂O₃(111)} complex in the presence of H⁺ and Cl⁻ ions are the attractive π–π stacking interactions between the aromatic rings and the delocalized electronic π cloud of the single molecule. The presence of aromatic (π-electrons) rings, gives the possibility of π-bond formation.

The negative and larger absolute value of adsorption energy for {141RR/α-Fe₂O₃(111)} complex under acidic conditions indicated that the corresponding adsorbed state is thermodynamically stable and reflects the spontaneity of the adsorption process. Energies of adsorption of the most stable geometry for {141RR/α-Fe₂O₃(111)} complex under acidic conditions is E_{ads} = -418.2512 Kj/mol, the contribution of the van der Waals interactions in stabilization of the complex is E_{vdW} = -42.4535 Kj/mol, beside this, the value of desorption energy is E_{desorption} = -418.2512 Kj/mol. The high value of energy of adsorption (-418.2512 Kj/mol) implied that we have a chimiosorption phenomenon.

4.2 RDF functions

To determine the structural characteristic of {RR141/α-Fe₂O₃(111)} system, we need to calculate the radial distribution functions (RDF) [42-44]. It's defined as the finding probability of a pair of particles (A&B) at a distance r apart, relative to the probability expected for an entirely random distribution at the same density. The RDF is calculated according to the following equation.

\[
g_{AB}(r) = \frac{1}{\langle \rho_B \rangle N_A} \sum_{i \in A} \sum_{j \in B} \frac{\delta(r_{ij} - r)}{4\pi r^2}
\]

\(<\rho>_B\) means the species density of B averaged over all shells around A species. The g_{AB}(r) parameter reflects the type of interaction (physio- or chemo-sorption) between the mineral surface and adsorbates. Particularly, the typical bond length of physisorption is greater than 3.5 Å much longer than chemical interaction types, which fall in the range of 1 Å–3.5 Å [43-44]. The structure {RR141/α-Fe₂O₃(111)} in the MD simulation systems (Fig. 5) can be presented by g_{AB}(r) parameter, such as iron-sulfur (g_{Fe-S}), iron-oxygen (g_{Fe-O}), iron-carbon (g_{Fe-C}), iron-nitrogen (g_{Fe-N}) and iron-chlorine (g_{Fe-Cl}) RDF. The values of the g_{AB}(r) are grouped in Table 2. According to the analysis of this table, it is very evident that the majority of the interatomic distance values are less than ≤3.55 Å, except for g_{Fe-088}, g_{Fe-094}, g_{Fe-100}, g_{Fe-0102}, g_{Fe-0116}, g_{Fe-0118} and g_{Fe-0123} distances RDFs, indicating a strong adsorption on the α-Fe₂O₃(111) surface, so we have a chemo-sorption of RR141 on Hematite α-Fe₂O₃(111). The obtained result show that the Hematite material can been a potential material to eliminate the RR141 azo dye from textile wastewater.
Conclusion

The theoretical investigation using DFT calculations and MD simulations carried out on the RR141, Hematite $\alpha$-Fe$_2$O$_3$ (111) and complex RR141/Hematite $\alpha$-Fe$_2$O$_3$ (111) indicate the following points: the Azo ($\text{N}_{77}$-$\text{N}_{71}$, $\text{N}_{16}$-$\text{N}_{30}$), hydroxy (-OH) and sulphonic acid (-SO$_3^-$) ions groups of reactive red dye (RR141) are the most reach sites of electron donor, so this area is most suitable to interact with minerale surface. The RR141 molecule adopts a parallel configuration over the minerale surface $\alpha$-Fe$_2$O$_3$ (111). The interfacial interaction is dominated by the hydrogen bonds and the interactions between Fe and hetero-atoms. The main driving force for the adsorption for \{141RR/$\alpha$-Fe$_2$O$_3$(111)\} complex is the attractive $\pi$–$\pi$ stacking interactions between the aromatic rings and the delocalized electronic $\pi$ cloud of the single molecule. The adsorption energy and RDF results indicate a strong interaction between organic compound RR141 and minerale surface of Hematite $\alpha$-Fe$_2$O$_3$ (111), revealing a chemo-sorption phenomena leading to a strong adsorption.
Conflicts of interest/Competing interests The authors declare that they have no conflict of interest and no competing interests exist.

Declarations Funding The authors received no specific funding for this work.

Ethics approval The manuscript is prepared in compliance with the Ethics in Publishing Policy as described in the Guide for Authors.

Consent to participate The manuscript is approved by all authors for publication.

Consent for publication The consent for publication was obtained from all participants.

Availability of data and material All data generated or analyzed during this study are included in this published article.


33. Crystal texture-dependent magnetic and magnetotransport properties of half-mineral Fe3O4 films grown on oxidized Si substrates by reactive deposition. J. Alloys Compd. 815, 152398 (2020).


Figures

Figure 1

2D structure of RR141
Figure 2

a: electronic density plot for LUMO of RR141 minimized structure in vacuum at B3LYP/6-31++G(d,p)

b: electronic density plot for HOMO of RR141 minimized structure in vacuum at B3LYP/6-31++G(d,p)

Electronic density plot for LUMO and HOMO of RR141 minimized structure in vacuum at B3LYP/6-31++G(d,p)
Figure 3

MEPs for the anionic Azo dye-Red RR141 molecule (Red: Strongly negative; Yellow: Moderately negative; Blue: Strong positive; Green: Moderately positive EP).
Figure 4

Top (left) and side (right) views for equilibrium configurations for \{141RR/\alpha-Fe_2O_3(111)\} complex under acidic conditions under normal pressure & ambient temperature

Figure 5

Relaxed adsorption geometries of the RR141 on \alpha-Fe_2O_3 (111) in parallel

\(Fe = \text{grey}; \ 0 = \text{red}; \ N=\text{blue}; \ S=\text{yellow}; \ C = \text{green and } H = \text{white.}\)

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