
| RESEARCH ARTICLE

Molecular Simulation of NaF Chemisorption on Lepidocrocite for Water Purification

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| ABSTRACT

NaF chemisorption onto lepidocrocite (LEP) was examined by experimental, molecular dynamics and DFT approach. DFT theoretical calculations suggest that the Fe and O atoms (OH species, for that matter) are the dominant active sites for the subsequent reaction on the LEP (0 0 1) surfaces. The adsorption of F onto LEP was relatively more favorable in acidic media compared to basic and neutral media and validated by experimental findings. The NaF adsorption sites vary in different media. The preferential adsorption of F onto LEP surfaces in acidic media was because of stable and strong interaction and/or thermodynamic stability between F adsorbate and the surface Fe and O atoms of LEP substrate.

| KEYWORDS

Clean water; Molecular dynamics simulation; Adsorption; Public health; Water purification; Fluoride removal

| ARTICLE INFORMATION

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1. Introduction

The discharge of fluoride-containing wastewaters from industries without treatment into natural surface and groundwater lead to fluorosis of the teeth and bones when these waters are consumed [Emamjomeh, 2016]. Due to the gradual increase in the world's population and water consumption, numerous current and future water shortage challenges are predicted by researchers. It has therefore become prerogative for researchers to find low-cost and environmentally friendly water treatment technologies to effectively handle water and groundwater for domestic consumption and wastewater generated from industries (before release into water bodies). In most parts of the world, the use of chemical coagulants (CC) to purify potable water is common and requires the additions of large amounts of aqueous solutions of Aluminum or Iron coagulants, presenting high maintenance and operational costs. Electrocoagulation (EC) (the generation of coagulants by dissolution of anodes to form metal hydroxides for treating wastewater) is therefore widely found to be a more effective alternative to CC in several studies in terms of total cost, energy consumption, chemical use, and metallic sludge disposal [Eskibalci, 2018; Martín-Domínguez, 2018]. Thus, EC research for wastewater treatment has garnered some attention [Mollah, 2010]. The electro-generated coagulants are large surface in area for rapid adsorption of suspended particles.

Molecular modeling is a quick way to examine the adsorption mechanism between pollutants and adsorbents to ease laboratory experiments by validating or eliminating prior experimental conclusions. Herein, a molecular level study to understand the interaction between Fe hydroxide (lepidocrocite) adsorbent surfaces and fluoride adsorbate was reported. Forcite molecular dynamic calculations using the adsorption locator module was used to analyze the interaction mechanisms between fluoride and LEP adsorbent based on experimental findings. Additionally, DFT approach was used to calculate the density of states (DOS) of the (0 0 1) face of LEP. This theoretical approach provides useful information on adsorption and interaction of F on lepidocrocite adsorbent.

2. Methodology

A 90 cm³ batch EC reactor was self-designed and constructed with Pyrex glass to the following dimensions: Two rectangular plates (Fe and Al) both 125 mm×45 mm×2 mm, with 45 cm² effective surface area were used as electrodes. The electrodes were placed in 60 cm³ of electrolyte and connected to an alternating rectangular pulse current power supply. EC operating times were set to 15, 20 and 30 min. The current densities 1 mA/cm², 2 mA/cm² and 3 mA/cm² were maintained for the alternating rectangular pulse currents, thus, producing a constant rate of metal cation dissolution. At the end of EC treatment, the adsorption yield (%) of F was calculated;

$$R (\%) = (C_0 - C) / C_0 \times 100\% \quad (1)$$

Where C_0 is the concentration before treatment and C is the concentration after treatment, which was obtained by measuring the potential and fitting to a fluoride ion standard concentration curve in Fig 3(a).

2.1 Molecular modeling and dynamic simulations

The low configuration adsorption energy (E_{ads}) of the F interactions onto the lepidocrocite adsorbent was calculated using various MD modeling modules. DFT Castep, Forcite and adsorption locator modules in Material Studio 2020 were employed to build adsorbent-adsorbate supercells. The most stable AC (001) surface was chosen for this simulation. The molecular simulation tasks were performed using a COMPAS II force field with an NVT canonical ensemble at 298 K. For the adsorption locator studies, the simulation box included 1 fluoride ion, 7 H₂O, 1 H⁺, and 1 Cl⁻ for acidic media, 7 H₂O, 1 HO⁻, 1 Na⁺ for basic media, and 8 H₂O simulating neutral media. The NaF-LEP(001) adsorption (E_{ads}) was evaluated as Eq. (2);

$$E_{ads} = E_{NaF-LEP(001)} - (E_{LEP(001)} + E_{NaF}) \quad (2)$$

3. Results and Discussion

3.1 Characterization and properties of adsorbents

Figure 1 shows the SEM-EDS and XRD analysis of mineral compositions of the electro-generated adsorbents under various initial pH conditions and current types. The SEM shows a highly dense or compact sludge, resembling dense clay soil layers. EDS analysis shows Fe adsorbents predominate the Al counterparts, possibly due to the many phases of Fe and their ability to transform into other phases. In accordance, a previous study [Fu, 2018] reported higher Fe(III) than Al³⁺ after synchronous periodic reversal EC treatment, indicating that Fe adsorbents were predominant during Fe/Al EC. The XRD shows wide peaks which are consistent with LDHs and GRs structures, which normally occur at low 2-theta ranges [Xie, 2017] due to pulse current leading to precipitation reactions between Fe(II,III)/Al³⁺/OH⁻.

Blue heat map analysis representing the effect of initial pH and electrolysis time on adsorbent generation is shown in Figure 1(c). As expected, increasing the current density as well as the electrolysis time increases the Fe/Al adsorbent production, with increasing pH. The reason is that, when pH value is higher than 6.0, the number of OH⁻ in solutions can easily precipitate with Fe²⁺ and Al³⁺ on Fe-Al LDHs structure [Xie, 2017]. This could explain the increase in adsorbent growth and the high yields obtained at pH 8. The applied current density directly affected the treatment efficiency in the electrochemical process by not only determining the production rates of adsorbents, but also changing the size and pace of bubbles produced, thus affecting the growth of the electrochemical adsorbents [Ren, 2011].

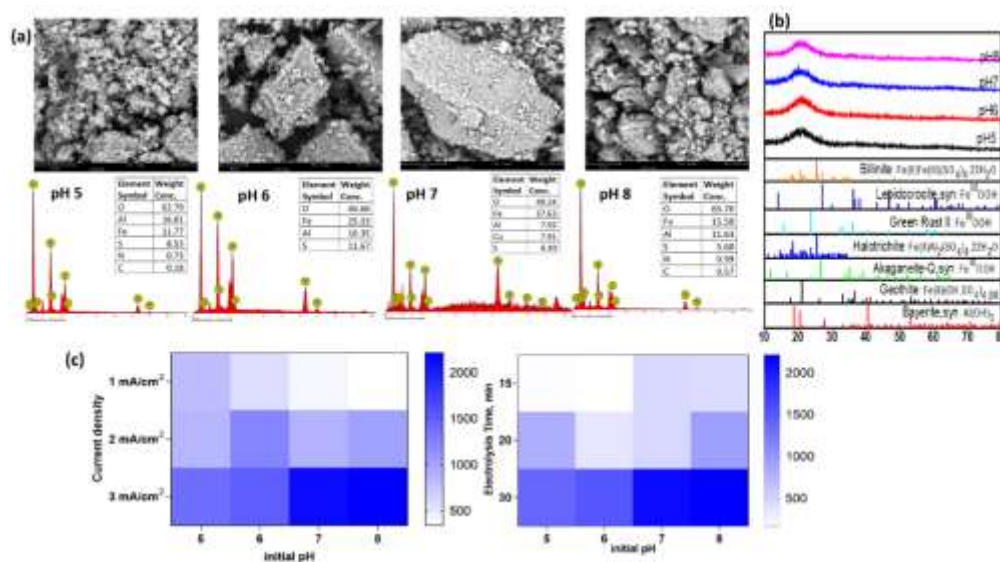


Figure 1. (a) SEM morphology and EDS elemental composition of Fe/Al adsorbents ($t = 30$ min, constant $j = 3$ mA/cm²) (b) XRD diagram of Fe/Al adsorbents under different initial pH. (c) Blue heat map showing yield of Fe/Al adsorbents produced under different (a) current densities after $t = 30$ min (b) time intervals

Figure 2(a, c) shows the adsorbate-adsorbent removal scenarios. F removal was favorable under a wide range of pH and is less influenced by initial pH conditions. The adsorption was higher at acidic and neutral pH, and the removal is attributed to adsorption mechanisms resulting from surface complexation reactions with hydroxides [Mollah, 2010; Golder, 2006]. Monomeric and polymeric Fe/Al hydroxide adsorbents are formed depending on solution pH during hydrolysis reactions. In the case of Al, precipitation occurs at low pH = 4.0–6.5 and adsorption by Al species are effective at pH > 6.5. In the case of Fe, good removal efficiencies were achieved at pH = 6–8 [Zongo, 2009 ; Eyvaz, 2014]. The slightly lower adsorption at basic medium implies that the rate of formation of metal–fluoride/fluoride–complexes may be lower due to solubility effects [12]. The adsorption of fluoride pollutants did not depend directly on the duration for which hydroxyl and metal ions are produced at the electrodes, as evidenced by effect of electrolysis time (Figure 2c). Increasing electrolysis time did not improve F adsorption. Figure 2b shows that water pH consecutively increased at all initial pH during the 30 min of EC process, implying the possible release of OH⁻ in solution caused by the ion exchange of F and OH⁻ species. The final pH increase for F adsorption can also be explained by the formation of OH⁻ from the reduction of H⁺ or H₂O on the surface of the cathode.

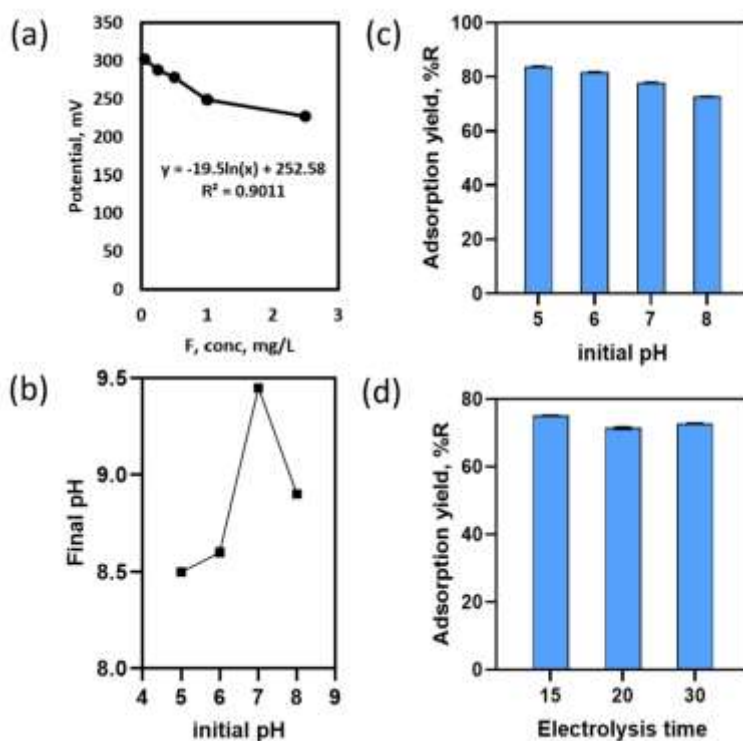


Figure 2. (a) Standard curve for fluoride determination (b) Final pH after fluoride adsorption (c, d) pH and electrolysis time effect on adsorption of fluoride

DFT theoretical calculations were used to elucidate the possible species of lepidocrocite involved in the fluoride adsorption. DFT computations were performed with LDA CA-PZ functional. The energy cutoff was 450 eV and the norm conserving pseudopotential was employed [Aguayo-Villarreal, 2020; Tong, 2018]. Figure 3 shows the TDOS and PDOS of atoms of the bulk LEP surfaces. The TDOS of LEP is mainly contributed to by the valence electrons of Fe and O atoms and in the valence band section, the 3d orbital of Fe and 3p and 4s orbitals of O presented an obvious overlap, indicating a forceful bonding between them. Additionally, the DOS at the Fermi level is largely occupied by the Fe 3d orbital. The O 3p orbitals also contributes to the DOS at the Fermi level. Both the Fe 3d and O 3p orbitals crossed the location of the Fermi level, suggesting that the Fe and O atoms (OH species for that matter) will be the dominant active sites for the subsequent reaction on the LEP (0 0 1) surfaces [Aguayo-Villarreal, 2020; Tong, 2018].

3.2 Adsorbate-adsorbent interaction

A wide variety of Fe adsorbents were generated by the alternating rectangular pulse current compared to Al adsorbents as shown in the XRD diagram in Figure 1. Thus, we decided to investigate the adsorption of F on lepidocrocite faces on the molecular level. Simulated annealing using the adsorption locator module of Materials Studio (2020) showed the lowest energy configuration of distances (r) between F ions and the surface ions of lepidocrocite and sulfate green rust in various media, as shown in Figure 4(a-l). The surface of LEP is composed of Fe and O-H species. The distance between F and the surface species were smallest in acidic medium, generating the most dominant adsorption sites (Assuming that the adsorption capacity is mainly contributed to by the dominant adsorption sites, which are the locations where the fluoride (adsorbate) is adsorbed onto lepidocrocite (0 0 1) face (adsorbent) (see Figure 4(a-e) and Table 1), then the adsorption capacity in acidic medium is higher compared to basic and neutral mediums. Therefore, the interaction between the adsorbate and the adsorbent mainly depends on the interaction between F and the lepidocrocite Fe and OH species. This observation aligns well with experimental results, which means the adsorption of F is stronger in acidic medium.

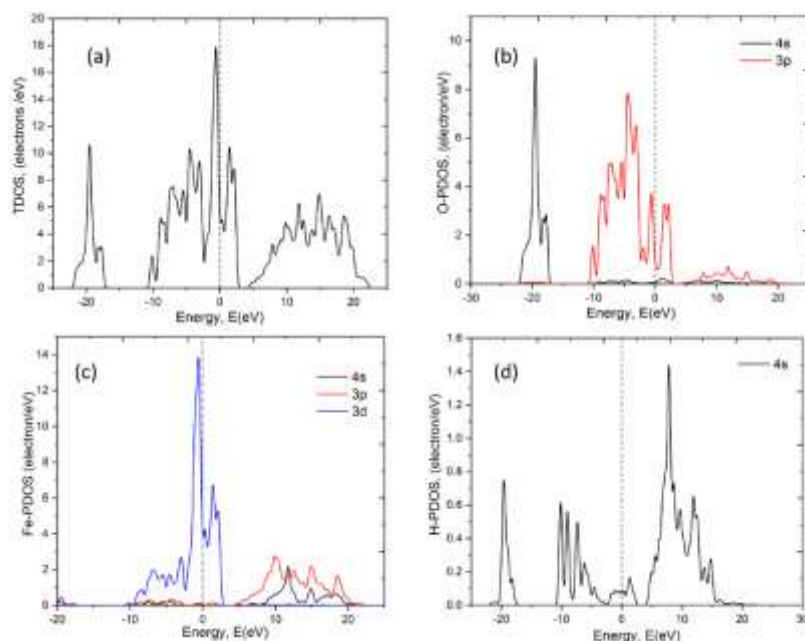


Figure 3 (a) Total density of states (TDOS) and (b-d) PDOS of bulk LEP

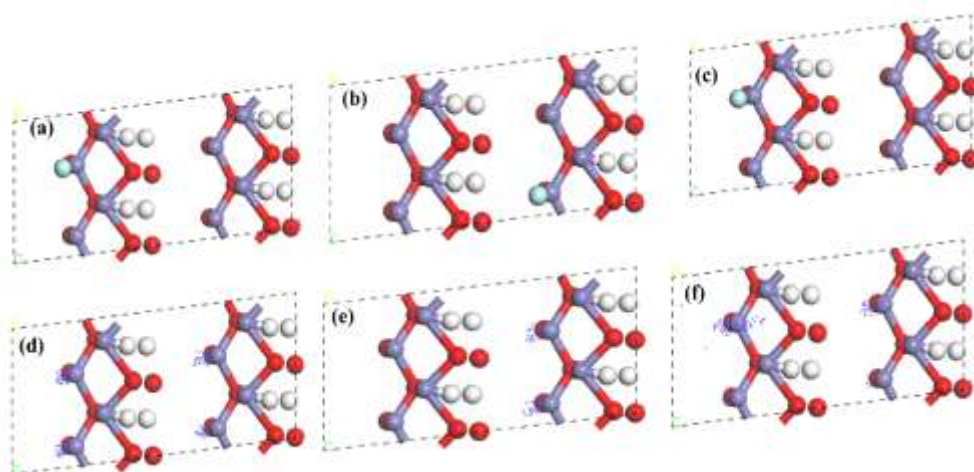


Figure 4. Adsorption site configuration (a-c) and adsorption density field (d-e) for F on lepidocrocite (0 0 1) surfaces in different media (O = red, Fe = violet, F = green, H = white).

Table 1. Adsorption sites and adsorption densities of F-LEP(001) system.

	Adsorption site	Adsorption density(max)
Neutral	Top Hole	3.37
Acidic	Top Hole	5.42
Basic	Top	4.58

After locating the adsorption sites, MD simulations were used to calculate the adsorption energies (E_{Ads}) and probability energy P(E) distribution, which provide a way to quantify the adsorption capacity of lepidocrocite for fluoride adsorbate. Table 2 shows the E_{Ads} obtained using the lowest energy configurations by adsorption locator calculations of NaF on LEP (0 0 1) surface in acidic, neutral and basic solutions. All E_{Ads} values are negative to show that the adsorption of NaF onto LEP is exothermic and spontaneous, and could be physicochemical or chemisorption in nature.

The adsorbate-adsorbent E_{Ads} is -147.94 kcal/mol in basic medium, -146.73 kcal/mol in acidic medium, and -146.05 kcal/mol in neutral medium. The more negative the adsorption energy, the easier the adsorption capacity of LEP in that medium. Figure 5

shows the probability energy $P(E)$ distribution for NaF-LEP interaction in different media; here, NaF-LEP exhibited the highest $P(E)$ of 2.26 in acidic media, 1.83 in basic media and 1.70 in neutral media such that the adsorption of F onto LEP is relatively more favorable in acidic media compared to basic and neutral media, and validated by experimental findings. This indicates a preferential adsorption of F onto LEP surfaces in acidic media as a result of stable and strong interaction and/or thermodynamic stability between F adsorbate and the surface Fe and O atoms of LEP substrate.

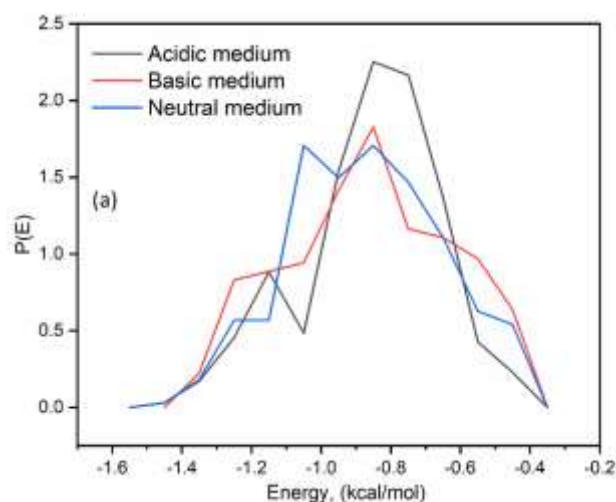


Figure 5. Probability energy distribution for F on LEP (0 0 1) surfaces in different media.

Table 2. Lowest energy parameters of stable configurations for F/LEP systems obtained from the adsorption locator calculations

Medium	E_{Total}	E_{Ads}	RAE	E_{def}	F : dE_{Ads}/dN_i	H_2O : dE_{Ads}/dN_i	H : dE_{Ads}/dN_i	OH : dE_{Ads}/dN_i
Neutral	-14.06	-146.05	-14.06	-131.99	-1.10	-18.15	-	-
Acidic	-14.73	-146.73	-14.73	-131.99	-1.18	-18.01	-0.60	-
Basic	-15.95	-147.94	-15.95	-131.99	-0.58	-18.17	-	-1.05

4. Conclusion

Molecular modeling was used to examine the adsorption mechanism of NaF chemisorption onto lepidocrocite to validate prior experimental conclusions. Forcite MD simulation and simulated annealing calculations in the adsorption locator was used to analyze the interaction mechanisms between fluoride and lepidocrocite adsorbent based on experimental findings. DFT theoretical calculations showed the possible species of lepidocrocite involved in the fluoride adsorption are the Fe and O atoms (OH species for that matter) and are the dominant active sites for the subsequent reaction on the LEP (0 0 1) surfaces. The adsorption of F onto LEP was relatively more favorable in acidic media compared to basic and neutral media and validated by experimental findings. The preferential adsorption of F onto LEP surfaces in acidic media was because of stable and strong interaction and/or thermodynamic stability between F adsorbate and the surface Fe and O atoms of LEP substrate.

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