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Research Paper

Investigation of the Adsorption Mechanism of Halogenated Anions in Industrial Wastewaters by Mg/AL Hydroxide Double Layer

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Abstract: In the wastewater of many industrial plants and mining industries, there are halogen compounds such as chlorine, fluorine, bromine and iodine, which can redce the quality of recycled water. One way to remove halogenated anions from wastewaters is to use layered double hydroxides, which have several advantages such as simplicity and low price. In this study, the adsorption properties of layered double magnesium / aluminum hydroxide is investigated by laboratory studies and molecular modeling for fluoride to iodine halogens. Laboratory studies have been performed to compare the ability to absorb different types of halogens by synthetic magnesium aluminum LDH (original and calcinated at 400 ˚C) and molecular modeling studies to understand effective mechanisms for different halogenated anions. The results of laboratory studies showed that both original and calcinated layered magnesium / aluminum hydrochloride have the highest absorption potential for fluoride ions and the lowest absorption for iodide ions. Calcination significantly increases absorption for all types of halogens. The predominant mechanism for the uptake of halogenated anions by non calcinated layered double hydroxides is ion-exchange and in calcinated products, surface and physical absorption. The electronegativity seems to be the determining parameter. The results of the energy calculation of the interaction obtained from the molecular modeling show that the preferred position for all halogens is the hollow hexagonal structure of the double-layer hydroxide. Also, the absorption rate in the hollow hexagonal position is the highest for the fluorine and the lowest for iodine. In addition to confirming the results of laboratory studies, these modelling results confirm the possibility of using molecular modeling methods as a powerful tool in examining the behavior and understanding the process mechanisms.

Keywords: Halogen, Adsorption, Double layer hydroxide, Molecular modeling.

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INTRODUCTION

Layered Double Hydroxides (LDH) are a group of compounds that have a brucite-like mineral structure ($Mg(OH)_2$) with a chemical composition of the general formula $[M_{1-x}^{+2}M_x^{+3}(OH)_2](A^{-n})_{x/n}mH_2O$. In LDH, a number of two-valent cation ions have been replaced by three-valent (M3 +) cations, resulting in a layered structure. These compounds are easily synthesized and have a permanent positive charge on the surface to absorb various anions. For this reason, in recent years, they have been proposed and used as effective attractions in various industries [1]. The anion adsorption mechanism depends on the nature of the adsorbent and the composition of the adsorbed anion. Layered double hydroxides can adsorb anionic species from the aqueous fluid medium through anion exchange as well as physical electrostatic adsorption. Anion adsorption is higher under slightly acidic conditions (typically pH 6) where there are more hydroxides in the insoluble double layered structure and fewer anions to compete [2]. Also, the higher the electronegativity of the anion, the higher its absorption rate in competition with other halogens [3].

In a recent study by Liu et al. In 2020, the structure and interaction of magnesium / aluminum double layered hydroxide surface with halogenated anions, hydroxide, carbonate, sulphate and phosphate were investigated by density functional theory [4]. The result of this study shows that the ion exchange sequence is $CO_3^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$. Also, the highest degree of interaction between the base orbitals of anions and magnesium cations is in the hydroxide structure. Despite the comprehensiveness of this study, due to the theoretical nature of this study, the adsorption rate trends for different anions in practice have not been validated with the results of molecular modelling results.

Despite numerous laboratory studies and some molecular modeling studies, the relationship between experimental adsorption data with molecular modeling results have not been studied so far [5-7]. In this research, the results will be compared by combining laboratory studies and molecular modeling while validating both methods. Also, in order to understand the effective mechanisms, the contribution of each including ion exchange and physical electrostatic absorption will be examined. Accurate understanding of the mechanism of adsorption of anions by double layered hydroxides leads to better synthesis of adsorbents as well as optimization of operating conditions of the adsorption process.

METHODS

In this research, studies were performed by two methods: laboratory studies and quantum molecular modeling.

Synthesis of layered double hydroxide

For the synthesis of hydroxide, the co-precipitation method proposed by Hong To Wang was used [8]. In this method, 7.6 g of 6-aqueous salt of Mg nitrate and 3.75 g of 9-aqueous salt of Al nitrate were dissolved in 250 ml of water. Then 24 g of caustic soda and 42.3 g of sodium carbonate in 300 ml of water were prepared (Merck). The two solutions were mixed together and then was stirred at 80 °C for 24 hours at a constant speed. The solution is then placed at room temperature for 3 to 4 days to precipitate. The resulting precipitate was filtered and washed with plenty of water to thoroughly wash out the nitrate in the precipitate. Finally, the sample was dried at 110 °C. Calcination was performed at 400 °C to investigate the effect of interlayer anions. At this temperature, carbonate interlayer is removed from the structure of LDH [2,8].

For adsorption experiments, a suspension with a concentration of 11 grams per 100 ml of the synthesized material was prepared. Halogen solutions were also prepared by potassium and sodium salts of these elements (KF, NaCl, KBr and KI). The test conditions were the same for all 4 samples, the temperature was about 30 to 40 °C for 4 hours on a magnetic stirrer, pH between 7 and 9 and ambient pressure. After adsorption tests on the two-layer hydroxides, the resulting solution was filtered and sent for analysis by ion chromatography.

In the modeling studies, the density functionall theory method and the Dmol3 tool was used in Materials Studio software version 2017 (developed by Accelerys, USA). Different structures of halogen deposition on the surface of hydroxide were investigated and after geomet optzation, the most stable deposition structure and interaction energy for F, Cl, Br, I were dound and calculated in COSMO media. The adsorption reaction energy (E_{ads}) was calculated from the following equation:

$$E_{ads}=E_{(H+LDH)}-[E_H + E_{(LDH)}] \quad (1)$$

where:

E_{ads} : the adsorption interaction energy

E_{H+LDH} : the total structural energy of the halogen on the hydroxide surface

E_{LDH} and E_{H} : are the structural energy of the LDH model and each of the halogens separately, respectively.

FINDINGS AND ARGUMENT

The X-ray diffraction spectra obtained from Mg/Al synthesized by the co-precipitation method in the molar ratio of aluminum to magnesium 1/2 and also its calcination product confirm the products are pure and well synthesized.

The adsorption results of the removal of halogenated anions by LDH are shown in Figure 1. The highest removal rate corresponds to fluorine ion and decreases towards iodine in the periodic column of halogens. The highest electronegative difference between fluorine atom and the cations on the surface of the hydroxide seems to be responsible for the observed trend. The greater the electronegativity difference between the halogenated anions and the surface cations, the greater the absorption.

The results of the calcinated sample show that calcination increases the removal of halogenated ions, which can be attributed to the removal of interlayer carbonate and the elimination of the competitive effect of halogenated ions with carbonate ions. Carbonate removal had the greatest effect on increasing the removal of fluoride in solution and the least number of changes for iodide ions.

The structure of magnesium / aluminum double layered hydroxide was modeled with carbonate interlayer anion and its structural parameters were calculated. Figure 1 shows the structure of the 2: 1 ratio of magnesium / aluminum hydroxide with the carbonate intermediate anion in the COSMO medium.

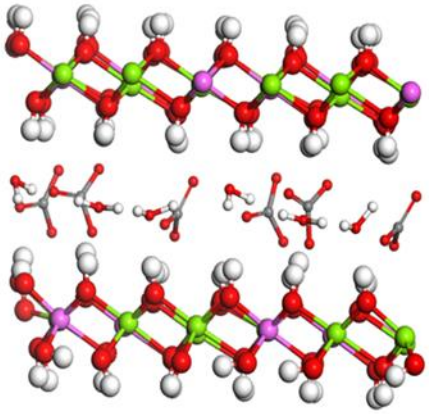

Figure 1. Image of the optimized structure of double layered hydroxide containing interlayer carbonate (The atoms are shown in aluminum, magnesium green, oxygen red, hydrogen white, and carbon gray.)

In order to compare the experimental results and molecular modeling in the optimized structure of carbonate containing carbonate, the interlayers of carbonate ions were removed and replaced with halogen ions. Figure 2 shows a comparison of the adsorption trend on calcined hydroxide obtained experimentally with the ratio of hydration energy to ionic radius obtained by modeling for halogens. To express the amount of halogen adsorption on the surface of hydroxide is bilayer and laboratory data confirms it.

CONCLUSIONS

The results of this study show that among different halogens, magnesium / aluminum double layered hydroxide has the highest adsorption for fluoride ion and the lowest adsorption for iodide ion. The trend of changes in the amount of halogen adsorption shows that both parameters of electronegativity are reflected in the amount of energy and ion hydration radius in molecular modeling and the ratio of charge to ionic radius is effective in the amount of halogen adsorption.

The predominant mechanism for the removal of halogens is physical adsorption in the case of calcined bilayer hydroxide and in the case of bilayer hydroxide containing anion between ions. Thermal activation associated with the removal of surface functional groups improves anion uptake. The preferred site for

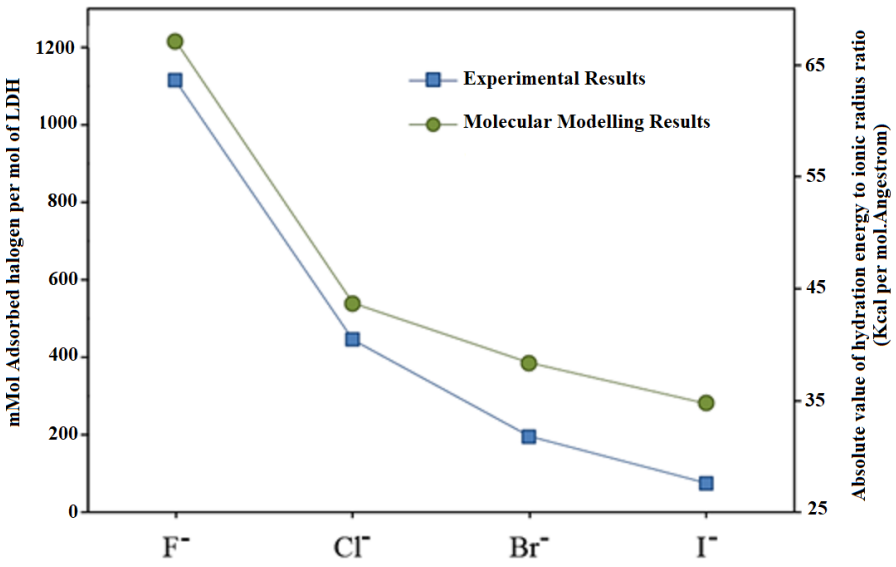

Figure 2. Comparison of experimental adsorption rate and ratio of hydration energy to ionic radius calcualted from molecular modeling results

adsorption of halogenated ions is at the hollow hexagonal surface. The reaction energy for the hollow quadrilateral position decreases from top to bottom in the halogens, which is consistent with the laboratory results of both physical adsorption and ion exchange. For the position of aluminum and magnesium, the trend of energy change is reversed and increases from top to bottom. The results of this study can be effective in understanding the exact mechanism of adsorption of anions by different adsorbents and finally the synthesis of suitable hydroxide for different anions.

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