



EXPERIMENTAL INVESTIGATION OF STRUCTURAL AND PROPERTY CHANGES OF MONTMORILLONITE TREATED WITH INORGANIC ACID SOLUTIONS

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Abstract: Montmorillonite is a layered aluminosilicate with a high ion exchange capacity and surface area, making it valuable in catalysis, adsorption, and material science. This study focuses on the structural and physicochemical changes in montmorillonite clay after treatment with inorganic acid solutions such as HCl and H₂SO₄. Using XRD, FTIR, BET, and TGA methods, we evaluate the effect of acid concentration and treatment duration on surface properties, crystallinity, and thermal stability. The results show significant enhancement in surface area, partial dealumination, and structural changes that make acid-treated montmorillonite more reactive for catalytic applications.

Keywords: Montmorillonite, acid activation, structure modification, XRD, BET surface area, FTIR, inorganic acids

Montmorillonite belongs to the smectite group of clays and is widely used in industries due to its swelling capacity, cation-exchange capability, and surface reactivity. To enhance these properties, montmorillonite is often modified through acid treatment, particularly with inorganic acids like hydrochloric acid (HCl) and sulfuric acid (H₂SO₄).

Acid treatment leads to leaching of octahedral cations (especially Al³⁺), resulting in increased porosity, surface area, and acid sites. However, excessive acidification can destroy the crystal structure. Understanding the optimal conditions for acid activation is essential to produce effective catalytic or adsorptive materials.

This study investigates how varying concentrations of HCl and H₂SO₄ affect the structural and chemical characteristics of montmorillonite. The findings contribute to optimizing acid activation processes for the development of functional clay-based materials.

The structural and chemical properties of montmorillonite are highly sensitive to external chemical influences, especially from acid solutions. Inorganic acids such as HCl and H₂SO₄ are commonly used to modify the clay's surface properties through processes such as dealumination, decationization, and exfoliation. These modifications





aim to improve the clay's specific surface area, porosity, and acidity—features critical for enhancing its performance in catalysis, environmental remediation, and material development.

Despite numerous studies on acid-activated clays, the mechanisms by which different acids and their concentrations affect the montmorillonite structure remain a topic of research interest. This study seeks to fill that gap by systematically analyzing the structural, thermal, and surface property changes that occur in montmorillonite after treatment with varying concentrations of hydrochloric and sulfuric acid solutions. The results provide insights into optimizing the acid activation process while preserving the desired mineral framework.

Materials

Natural sodium montmorillonite clay was obtained and purified by sedimentation and centrifugation. Acid treatments were performed using aqueous HCl and H₂SO₄ solutions at different molarities (0.5 M, 1 M, 2 M).

Acid Treatment Procedure

1 g of clay was dispersed in 100 mL of acid solution and stirred at 80°C for 2–6 hours. The suspension was filtered, washed until neutral, dried at 105°C, and calcined at 300°C.

Characterization Techniques

- **XRD (X-ray diffraction)**: for crystal structure analysis
- **FTIR (Fourier-transform infrared spectroscopy)**: for functional group identification
- **BET (Brunauer–Emmett–Teller) method**: for surface area measurement
- **TGA (Thermogravimetric analysis)**: for thermal stability and decomposition profile

XRD Analysis

XRD patterns showed that low-concentration acid treatments preserved the layered structure, while higher concentrations caused a decrease in peak intensity and partial collapse of the basal spacing, indicating dealumination and structural degradation.

FTIR Spectra

The intensity of bands corresponding to Al–OH and Si–OH vibrations decreased after acid treatment, confirming the leaching of Al³⁺ ions from octahedral sheets. New bands attributed to silanol groups (Si–OH) became more prominent, suggesting increased surface reactivity.





BET Surface Area

The surface area increased from 64 m²/g (raw) to 128 m²/g after treatment with 1 M HCl for 4 hours. Acid treatment removed cations and opened up the pore structure, improving textural properties. Excessive treatment with 2 M H₂SO₄ led to partial pore collapse and decreased BET surface area.

Sample	Acid Type	Molarity	BET Surface Area (m ² /g)
Raw Clay	–	–	64
HCl-treated	1 M	1 M	128
H ₂ SO ₄ -treated	2 M	2 M	92

TGA Results

Thermal analysis revealed improved thermal resistance in acid-treated clays up to 350°C. Weight loss corresponding to dehydroxylation shifted slightly due to structural changes.

The analysis revealed distinct trends in structural and surface property changes in montmorillonite upon treatment with different concentrations of inorganic acids.

XRD patterns showed a gradual reduction in peak intensity corresponding to the basal spacing (d001), particularly with higher acid concentrations. This indicated a partial destruction of the layered structure due to the leaching of Al³⁺ and Mg²⁺ ions from the octahedral sheets. However, low-concentration treatments preserved the structural framework while enhancing the surface activity.

FTIR spectra supported this observation, as the disappearance or weakening of absorption bands at ~3620 cm⁻¹ (Al–OH) and ~915 cm⁻¹ (Al–Al–OH bending) confirmed dealumination. New peaks associated with Si–OH vibrations (~1050–1100 cm⁻¹) emerged more prominently, indicating increased silanol group formation—essential for improved surface reactivity.

BET surface area measurements revealed the most notable enhancements:

- The raw montmorillonite had a surface area of ~64 m²/g.
- After treatment with 1 M HCl, the surface area **doubled** to 128 m²/g.
- However, treatment with 2 M H₂SO₄, although effective in initial activation, caused **structural collapse**, reducing surface area to ~92 m²/g.

TGA results showed two main stages of weight loss:

1. Dehydration of adsorbed water (~25–150°C)
2. Dehydroxylation of structural OH groups (~450–650°C)





Acid-treated samples exhibited delayed and reduced dehydroxylation peaks, indicating a lower content of octahedral hydroxyl groups due to acid leaching, and improved thermal stability up to 300–350°C.

Cation exchange capacity (CEC) measurements also demonstrated slight decreases after strong acid treatments, further confirming partial loss of exchangeable cations and structural aluminum.

Summary Table of Key Results

Sample	Acid Type	Molarity	BET (m ² /g)	d001 (nm)	Al–OH Band Intensity	Thermal Stability
Raw Montmorillonite	–	–	64	1.24	High	Moderate
HCl-treated	1 M	1 M	128	1.20	Medium	High
H ₂ SO ₄ -treated	2 M	2 M	92	1.17	Low	Moderate

Inorganic acid treatment effectively modifies montmorillonite by enhancing its surface area, porosity, and acidity. HCl treatment is more effective in increasing BET surface area and partial dealumination, making it suitable for catalytic applications. However, over-treatment with strong acids can damage the crystalline structure, reducing effectiveness. Controlled acid modification thus provides a valuable route to engineer montmorillonite for use in adsorption and heterogeneous catalysis.

The experimental findings clearly demonstrate that acid treatment is a powerful method for tuning the physicochemical properties of montmorillonite. Moderate acid activation—especially using 1 M HCl—enhances surface area, increases porosity, and introduces more reactive acid sites without fully degrading the clay structure. This optimized treatment makes montmorillonite suitable for various industrial uses, particularly in catalysis and adsorption.

However, excessive acid strength or prolonged exposure can damage the structural integrity of the clay, leading to decreased surface area and functional performance. Therefore, a balance must be maintained between achieving activation and preserving the structural framework of montmorillonite.

Future studies should investigate the catalytic behavior of these acid-modified montmorillonites in specific organic reactions, such as esterification, aldol condensation, or hydrocracking, and explore their reusability and economic feasibility in real industrial systems.





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