EFFECTIVE METHODS OF VERMICULITE MINERAL MODIFICATION: ACID, ALKALINE, AND THERMAL TREATMENTS

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ABSTRACT

Vermiculite is a layered magnesium aluminium silicate whose high cation exchange capacity, thermal expansibility and chemical inertness make it an attractive precursor for functional adsorbents, catalysts and thermal insulation fillers. The present study examines the physicochemical evolution of vermiculite subjected to three widely employed modification routes—acid leaching, alkaline activation and rapid thermal exfoliation—and compares their efficacy in generating surface area, porosity and functional surface groups. Samples of crude Tebinbuloq vermiculite were treated with 25 % H_2SO_4 at 95 °C for 6 h, with 1.5 M KOH at 60 °C for 24 h, and by flash heating to 850 °C for 5 min. X ray diffraction, FTIR spectroscopy, BET nitrogen adsorption and ICP OES were used to track structural and compositional changes, while Cu^{2+} uptake from aqueous solution provided an integral performance metric. Acid treatment produced a two fold rise in BET surface ($61 \rightarrow 128\ m^2\ g^{-1}$) through dealumination and silica skeleton formation; alkaline attack enhanced microporosity and generated reactive $–Si–O^-$ sites that boosted cation exchange capacity to $155\ mmol\ kg^{-1}$; thermal exfoliation yielded the largest pore volume ($0.51\ cm^3\ g^{-1}$) and a six fold decrease in bulk density, facilitating rapid intraparticle diffusion.

KEYWORDS

Vermiculite; acid activation; alkaline activation; thermal exfoliation; adsorption; Tebinbuloq deposit.

INTRODUCTION

Vermiculite, a 2:1 phyllosilicate belonging to the trioctahedral mica group, consists of negatively charged sheets of $(Si,Al)O_4$ tetrahedra balanced by interlayer Mg^{2+}, K^+ and exchangeable hydration water. On heating above 600 °C the interlayer water vaporises and forces the sheets apart, yielding the hallmark accordion like morphology exploited in lightweight insulation and horticultural substrates. Beyond these bulk uses, interest has shifted toward high value environmental applications—particularly metal and dye adsorption, catalytic supports and controlled release matrices—where performance is dictated by surface chemistry, layer accessibility and diffusion pathways. Native vermiculite from Tebinbuloq, like many deposits, exhibits a modest specific surface ($50–70\ m^2\ g^{-1}$) and limited microporosity; unlocking its potential therefore requires post mineral treatments that selectively remove or reorganise structural elements.

Three modification strategies have proven especially effective. Acid attack, generally with mineral acids, dissolves octahedral Mg^{2+} and part of the Al^{3+} framework, producing amorphous silica, expanding interlayers and generating Brønsted acid sites. Alkaline activation with concentrated hydroxides promotes layer delamination through Si O Si cleavage and creates nucleation centres for subsequent intercalation or organo functionalisation, while simultaneously elevating the cation exchange capacity. Thermal exfoliation, a purely physical route, instantaneously expands the lattice, multiplies pore volume and enhances diffusional accessibility without introducing foreign ions. Although the three routes are frequently described in isolation, comparative assessments on a single ore and under controlled laboratory conditions remain rare. This work therefore provides a side by side evaluation of acid, alkaline and thermal treatments applied to Tebinbuloq vermiculite, furnishing quantitative links between structural evolution and adsorptive behaviour.

Raw vermiculite (grain size 0.5–1 mm) was hand picked from Tebinbuloq mine stockpiles, washed, oven dried at 105 °C and milled to <75 µm. Acid activation employed a 1:5 solid to liquid ratio in 25 % H_2SO_4 under reflux at 95 °C for six hours, followed by repeated decantation until pH $\approx$ 6 and drying at 80 °C. Alkaline treatment used 1.5 M KOH at 60 °C under vigorous stirring for 24 h; the slurry was neutralised with 0.01 M HCl, rinsed and dried as above. Thermal exfoliation was performed in a muffle furnace pre heated to 850 °C; 10 g aliquots were introduced in alumina crucibles and heated for five minutes before quenching in a desiccator.

Phase identity and lattice parameters were tracked by X ray diffraction (Cu Kα, 40 kV, 30 mA). Functional groups were probed by FTIR (400–4000 cm^{-1}, 64 scans). Specific surface area and pore distribution were determined from N_2 adsorption desorption isotherms at –196 °C using BET and BJH models. Elemental composition was analysed by inductively coupled plasma optical emission spectroscopy after lithium borate fusion. Bulk density of thermally expanded samples was measured by graduated cylinder tapping. Adsorptive performance was evaluated in batch mode with 50 mg of modified vermiculite contacted with 50 mL of 100 mg L^{-1} $CuSO_4$ solution at pH 5.5, 25 °C, 180 rpm for two hours; residual Cu^{2+} was quantified spectrophotometrically. All measurements were carried out in triplicate, and average values are reported.

XRD patterns confirmed pronounced structural divergence among the three treatments. Acid leaching dramatically suppressed the (001) basal reflection and broadened high angle peaks, indicating partial delamination and amorphisation. ICP OES showed that MgO and Al_2O_3 contents dropped by 78 % and 46 % respectively, while SiO_2 rose to 72 wt %, consistent with selective octahedral stripping and silica skeleton enrichment. These changes translated into a BET surface area of 128 $m^2\ g^{-1}$ and a mesopore volume of 0.34 $cm^3\ g^{-1}$. The corresponding Cu^{2+} uptake reached 88 mg g^{-1}, attributed to the high density of silanol groups and newly created micropores borderlined by residual octahedral vacancies that act as coordination sites.

Alkaline activation preserved the layer periodicity but expanded the interlayer spacing from 1.44 to 1.52 nm, as inferred from the shifted basal peak. IR spectra revealed intensified $Si–O^{-}$ stretching at 989 cm^{-1} and diminished OH bending bands, pointing to deprotonation and partial silica de tetrahedralisation. Despite a modest BET increase to 104 $m^2\ g^{-1}$, the micropore fraction grew disproportionately, leading to a cation exchange capacity of 155 mmol kg^{-1}, almost double that of the raw mineral. Equilibrium sorption studies confirmed preferential binding of Cu^{2+} over Na^{+} or Mg^{2+}, endorsing the route for water treatment adsorbents where selectivity toward divalent contaminants is crucial.

Comparative evaluation thus suggests that treatment choice should follow the intended functional profile. For heavy metal immobilisation in industrial effluents, acid activated vermiculite offers superior capacity owing to abundant silanol nests and increased mesoporosity. When high ion exchange density is sought—for example in nutrient release fertiliser coatings—alkaline activation delivers the highest cation exchange sites while preserving structural integrity. Applications demanding rapid mass transfer with minimal pressure drop, such as fixed bed gas–solid adsorption, benefit most from thermally exfoliated vermiculite. The data also reveal synergy: a short alkaline pre treatment that weakens interlayer cohesion followed by flash exfoliation at 750–800 °C produced a hybrid material (tested in a pilot batch) combining 0.45 $cm^3\ g^{-1}$ total pore volume with 140 $m^2\ g^{-1}$ surface area, while retaining 80 % of the pristine layer charge. Such staged processing reduces acid consumption, shortens dwell time and meets increasingly stringent environmental regulations on effluent neutrality.

Systematic comparison of Tebinbuloq vermiculite modified by acid, alkaline and thermal routes shows that each treatment endows the mineral with a distinctive balance of porosity, surface chemistry and adsorption kinetics. Acid leaching maximises surface area and metal binding capacity through framework dealumination; alkaline activation boosts cation exchange density and interlayer accessibility; thermal exfoliation generates low density, high throughput structures ideal for flow through processes. An integrated alkaline thermal sequence emerges as a promising compromise, producing multifunctional sorbents with balanced capacity and mass transfer characteristics while reducing reagent and energy inputs. These findings provide a scientific basis for tailoring vermiculite derived materials to specific environmental and industrial applications and support the strategic utilisation of Uzbekistan's mineral resources.

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