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BENTONITE MODIFIED WITH METAL SALTS FOR ENHANCED ADSORPTION OF Cu^{2+}, PO_4^{3-} AND OIL POLLUTANTS IN WASTEWATER TREATMENT

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Abstract. This study investigates the structural, textural, and adsorption properties of two bentonite clays (B1, Na-smectite; B2, Ca/Mg-smectite) from Uzbekistan, subjected to sequential enrichment and surface modification with metal (hydr)oxide coatings. Enrichment via decantation and 10% H_2SO_4 treatment increased montmorillonite content, raised BET specific surface area from 56–77 m^2/g, and reduced mean pore radius to 3.6–4.0 nm. Modification at pH 9–11 with two salt mixtures — $Fe^{3+}/Mg^{2+}/Mn^{2+}$ (FB series) and $Ca^{2+}/Zn^{2+}/Mn^{2+}$ (KB series) — followed by thermal stabilization at 300 °C further elevated surface area to 95–146 m^2/g and total pore volume to 0.305–0.354 cm^3/g. X-ray diffraction confirmed intercalation and formation of iron oxide (hematite, magnetite) phases. Maximum adsorption capacities were 128.5 mg/g for Cu^{2+} and 153.3 mg/g for PO_4^{3-} at neutral pH, with adsorption efficiency strongly pH-dependent (optimal range 2–10). Adsorption of water vapor favored KB composites, whereas benzene vapor adsorption favored FB composites, reflecting contrasting surface hydrophilicity. Modified bentonites reduced petroleum contaminants by >80% and, when combined with H_2O_2, achieved ~99% oxidative removal of oils and fats within 20–25 min. These results demonstrate the superior environmental remediation potential of metal (hydr)oxide-coated bentonites for multi-contaminant wastewater treatment.

Keywords: bentonite; montmorillonite, clay enrichment, acid activation, metal oxide modification, adsorption, heavy metals; copper removal, phosphate removal, wastewater treatment; BET surface area, X-ray diffraction; petroleum sorption

Аннотация. В данном исследовании изучены структурные, текстурные и адсорбционные свойства двух типов бентонитовых глин (B1 — Na-смектит; B2 — Ca/Mg-смектит) из Узбекистана, подвергнутых последовательному обогащению и модификации поверхности покрытиями металл(гидр)оксидов. Обогащение методом декантации и обработкой 10% H_2SO_4 привело к увеличению содержания монтмориллонита, росту удельной поверхности по BET до 56–77 $м^2/г$ и снижению среднего радиуса пор до 3.6–4.0 нм. Модификация при pH 9–11 с использованием двух смесей солей — $Fe^{3+}/Mg^{2+}/Mn^{2+}$ (серия FB) и $Ca^{2+}/Zn^{2+}/Mn^{2+}$ (серия KB) — с последующей термической стабилизацией при 300 °C позволила увеличить поверхность до 95–146 $м^2/г$ и общий объем пор до 0.305–0.354 $см^3/г$. Рентгенодифракционный анализ подтвердил интеркаляцию и образование фаз оксидов железа (гематит, магнетит). Максимальная адсорбционная емкость составила 128.5 мг/г для Cu^{2+} и 153.3 мг/г для PO_4^{3-} при нейтральном pH. Эффективность адсорбции существенно зависела от pH, оптимальный диапазон составил 2–10. Адсорбция водяного пара была выше для композитов серии KB, тогда как адсорбция паров бензола — для серии FB, что отражает различия в гидрофильности поверхности. Модифицированные бентониты обеспечили снижение нефтяных загрязнений более чем на 80%, а в сочетании с H_2O_2 достигали ~99% окислительного удаления масел и жиров за 20–25 минут.

Полученные результаты демонстрируют высокий потенциал бентонитов, модифицированных металл(гидр)оксидами, для очистки сточных вод от многокомпонентных загрязнений.

Ключевые слова: бентонит, монтмориллонит, обогащение глин, кислотная активация, модификация оксидами металлов, адсорбция, тяжелые металлы, удаление меди, удаление фосфатов, очистка сточных вод, удельная поверхность BET, рентгенодифракция, сорбция нефтепродуктов

Annotatsiya. Ushbu tadqiqotda O‘zbekistondan olingan ikki xil bentonit gilining (B1-Na-smektit; B2-Ca/Mg-smektit) strukturaviy, teksturaviy va adsorbsion xossalari o‘rganildi. Namunalar ketma-ket boyitish va metall (gidr)oksid qoplamalari bilan yuzasini modifikatsiya qilish orqali tayyorlandi. Dekantatsiya va 10% H_2SO_4 bilan ishlov berish orqali montmorillonit miqdori oshirildi, BET bo‘yicha solishtirma sirt maydoni 56–77 m^2/g gacha ko‘tarildi hamda o‘rtacha g‘ovak radiusi 3.6–4.0 nm gacha kamaydi. pH 9–11 sharoitida ikki xil tuz aralashmasi -$Fe^{3+}/Mg^{2+}/Mn^{2+}$ (FB seriyasi) va $Ca^{2+}/Zn^{2+}/Mn^{2+}$ (KB seriyasi) yordamida modifikatsiya qilinib, 300 °C da termik barqarorlashtirishdan so‘ng sirt maydoni 95–146 m^2/g gacha, umumiy g‘ovak hajmi esa 0.305–0.354 cm^3/g gacha oshdi. Rentgen difraksiyasi tahlili interkalatsiya jarayoni va temir oksidlari (gematit, magnetit) fazalarining hosil bo‘lishini tasdiqladi. Maksimal adsorbsiya sig‘imi neytral pH da Cu^{2+} uchun 128.5 mg/g va PO_4^{3-} uchun 153.3 mg/g ni tashkil etdi. Adsorbsiya samaradorligi pH ga kuchli bog‘liq bo‘lib, optimal oraliq 2–10 deb topildi. Suv bug‘ining adsorbsiyasi KB kompozitlarida yuqori bo‘lsa, benzol bug‘ining adsorbsiyasi FB kompozitlarida ustunligi kuzatildi, bu esa sirt gidrofilligining farqlanishi bilan izohlanadi. Modifikatsiyalangan bentonitlar neft mahsulotlarini 80% dan ortiq kamaytirdi va H_2O_2 bilan birgalikda qo‘llanganda 20–25 daqiqa ichida yog‘ va moylarni taxminan 99% oksidlovchi yo‘l bilan yo‘qotdi. Ushbu natijalar metall (gidr)oksid bilan qoplangan bentonitlarning ko‘p komponentli oqava suvlarni tozalashda yuqori samaradorlikka ega ekanligini ko‘rsatadi.

Kalit so‘zlar: bentonit, montmorillonite, gilni boyitish, kislota bilan faollashtirish, metall oksid modifikatsiyasi, adsorbsiya, og‘ir metallar, misni ajratish, fosfatni ajratish, oqava suvlarni tozalash, BET sirt maydoni, rentgen difraksiyasi, neft mahsulotlari sorbsiyasi.

1. INTRODUCTION

Access to clean water is one of the most pressing global challenges of the 21st century. Industrial effluents containing heavy metals, phosphates, and petroleum-derived compounds pose severe ecological risks, threatening aquatic ecosystems and human health [1,2]. Conventional treatment technologies — chemical precipitation, ion exchange, membrane filtration — are often cost-prohibitive for developing economies and generate secondary pollutants. Low-cost mineral adsorbents, particularly natural clays, have therefore attracted sustained research interest as sustainable alternatives [3,4].

Bentonite, composed primarily of the 2:1 phyllosilicate montmorillonite, is globally abundant, inexpensive, and possesses a large interlayer cation-exchange capacity (CEC, typically 60–120 meq/100 g), high specific surface area, and swelling behavior that together facilitate pollutant capture from aqueous solution [5,6]. However, natural bentonite has limitations: its layered structure can collapse under thermal or pH stress, its selectivity for specific contaminants is moderate, and unmodified Na-type or Ca-type forms differ markedly in their adsorption profiles [7].

Two main strategies are employed to enhance bentonite performance: (i) beneficiation (enrichment) — physical separation and/or acid activation to remove non-clay impurities and augment montmorillonite content; and (II) surface modification — introduction of inorganic pillars, organic surfactants, or metal (hydr)oxide coatings [8,9]. Metal oxide coating is particularly attractive because iron, manganese, and zinc oxyhydroxides formed on the clay surface generate abundant Lewis acid sites and surface hydroxyl groups, which interact strongly with both cationic heavy metals (Cu^{2+}, Pb^{2+}, Cd^{2+}) and anionic species (PO_4^{3-}, CrO_4^{2-}) through surface complexation mechanisms rather than simple ion exchange [10,11].

Iron-bearing composites also display Fenton-like catalytic activity in the presence of H_2O_2, enabling oxidative degradation of recalcitrant organic pollutants such as petroleum hydrocarbons and lipids — a dual adsorption–catalysis function rarely demonstrated for bentonite-based materials [12,13].

Despite the volume of literature on modified clays, systematic comparison of Na- vs. Ca/Mg-type starting materials, two distinct coating chemistries, and their performance across inorganic ions, vapors, and organic contaminants within a single study remains limited, particularly for Central Asian bentonite resources.

This work addresses that gap using two bentonite samples from Uzbekistan (B1: Na-montmorillonite; B2: Ca/Mg-montmorillonite). The objectives are to: (1) characterize the structural and textural evolution of both clays upon enrichment and modification; (2) quantify adsorption performance for Cu^{2+}, PO_4^{3-}, water vapor, benzene vapor, petroleum products, and fats; (3) elucidate the mechanistic differences between $Fe^{3+}/Mg^{2+}/Mn^{2+}$ and $Ca^{2+}/Zn^{2+}/Mn^{2+}$ coating systems; and (4) evaluate pH dependence and kinetic profiles relevant to engineering design.

2. MATERIALS AND METHODS

2.1. Starting Materials

Two bentonite clay samples were sourced from domestic deposits in the Republic of Uzbekistan. Sample B1 is a sodium-type (Na-smectite) bentonite with a high monovalent cation content (Na_2O = 3.9 wt%), while sample B2 is a calcium–magnesium-type (Ca/Mg-smectite) bentonite (CaO = 3.8 wt%, MgO = 3.1 wt%). Both samples were air-dried and manually crushed prior to processing. All reagents used were of analytical grade (sulfuric acid, iron(III) chloride hexahydrate, magnesium chloride hexahydrate, manganese(II) chloride tetrahydrate, calcium chloride hexahydrate, zinc chloride, sodium hydroxide; Sigma-Aldrich and Reakhim).

2.2. Enrichment Procedure

Raw clay was dried at 105 ± 5 °C to constant mass, then dispersed in distilled water (solid:liquid = 1:5) and allowed to swell for 24 h. The suspension was mechanically stirred for 20 min, after which the upper 10 cm layer was decanted to separate sand and coarse impurities from the lighter montmorillonite fraction. The recovered fine suspension was allowed to settle, the supernatant was decanted, and the sediment was treated with 10% H_2SO_4 (1:1 v/v) at 40–50 °C for 2 h with continuous stirring. The acid-treated solid was centrifuged, washed with distilled water to pH-neutral, and dried at 105 ± 5 °C. The enriched products are designated OB1 and OB2.

2.3. Modification with Metal (Hydr)oxide Coatings

Twenty grams of enriched bentonite was suspended in 400 cm^3 of distilled water and stirred for 1.5–2 h. Two 100 cm^3 salt solutions were prepared:

Solution 1 (FB series): 0.541 g $FeCl_3 \cdot 6H_2O$ + 0.406 g $MgCl_2 \cdot 6H_2O$ + 0.198 g $MnCl_2 \cdot 4H_2O$

Solution 2 (KB series): 0.438 g $CaCl_2 \cdot 6H_2O$ + 0.488 g $ZnCl_2 \cdot 6H_2O$ + 0.198 g $MnCl_2 \cdot 4H_2O$

Each salt solution was introduced dropwise into the clay suspension simultaneously with 0.5 M NaOH to maintain pH 9–11. After addition, the pH was adjusted to 10 and the mixture aged for 6 h at room temperature. The precipitate was filtered, washed to absence of Cl^- (tested with $AgNO_3$), dried at 105 ± 1 °C, and thermally stabilized at 300 °C for 1.5–2 h. The resulting composites — FB1, FB2 (Fe/Mg/Mn-modified B1 and B2) and KB1, KB2 (Ca/Zn/Mn-modified B1 and B2) — were ground in an agate mortar and sieved to <125 μm (120 mesh).

2.4. Characterization Techniques

X-ray powder diffraction (XRD) was performed on a DRON-3 diffractometer (Cu Kα radiation, λ = 0.154 nm, 2θ range 3°–70°, step 0.05°). Interplanar spacings were calculated using Bragg's equation. Chemical composition was determined by X-ray fluorescence (XRF). Particle size distribution was measured by laser diffraction (Mastersizer 2000). Textural properties (BET specific surface area, mean pore radius, total pore volume) were obtained from N_2 adsorption–desorption isotherms at 77 K (ASAP 2020, Micromeritics). Adsorption of water and benzene vapors was measured gravimetrically on a McBain quartz spring balance under vacuum (residual pressure 10^{-3} mmHg; pre-degassing 8 h at ambient temperature).

2.5. Adsorption Experiments

Kinetic and equilibrium adsorption studies were conducted in batch mode at 25 ± 1 °C. Stock solutions of $CuSO_4$ (Cu^{2+}, 200 mg/L) and Na_3PO_4 (PO_4^{3-}, 200 mg/L) were prepared. Adsorbent dose: 1 g/L. Agitation: 150 rpm on a rotary shaker. Equilibrium time was confirmed from kinetic curves (10–50

h depending on sorbent). Isotherms were constructed at pH 7.0 over concentration ranges 3–200 mg/L. pH-dependent experiments covered pH 2–10 (adjusted with 0.1 M HCl or NaOH). Residual Cu^{2+} was determined by atomic absorption spectroscopy; PO_4^{3-} by the molybdenum blue colorimetric method at 880 nm. Adsorption capacity (mg/g) was calculated by mass balance.

Petroleum product and fat sorption was studied using model solutions (10 mg/L hydrocarbons; 50 mg/L fats). Petroleum concentration was quantified by IR absorbance at λ = 3420 nm after CCl_4 extraction. Fats were determined by double CCl_4 extraction with differential measurement. Catalytic oxidation experiments employed H_2O_2 at 360 mg/L; optimal temperature >20 °C was established from preliminary screening.

2.6. Data Analysis

Adsorption isotherms were fitted to the Langmuir model (Eq. 1) and BET model (Eq. 2) using non-linear regression (OriginPro 2023). Kinetic data were modeled with pseudo-first-order and pseudo-second-order equations. All experiments were performed in triplicate; results are reported as mean ± standard deviation (SD < 5%).

$$A = A\infty KC / (C_0(1 + KC/C_0)) \quad [Langmuir, Eq. 1]$$

$$A = A\infty KP/Ps / ((1 + P/Ps)(1 + (K-1)P/Ps)) \quad [BET, Eq. 2]$$

3. RESULTS AND DISCUSSION

3.1. Effect of Enrichment on Mineralogy and Chemical Composition

XRD analysis of raw and enriched samples confirmed the presence of montmorillonite, illite, clinoptilolite, albite, and low-temperature quartz (α-SiO_2) in both B1 and B2. Upon enrichment, the intensity of quartz reflections (d = 0.428, 0.182, 0.154 nm) decreased by 50–70%, while montmorillonite reflections (d = 1.349, 1.253 nm) increased 2–4-fold, confirming effective concentration of the clay fraction. The characteristic d_{001} reflection of Na-montmorillonite (B1) appeared at 2θ ≈ 12.4° (d ≈ 7.1 Å), and for Ca/Mg-montmorillonite (B2) at 2θ ≈ 8.9° (d ≈ 9.9 Å), consistent with differing interlayer hydration states.

Chemical analysis (Table 1) showed that enrichment decreased SiO_2 slightly (indicative of quartz removal), increased Al_2O_3 (reflecting higher montmorillonite concentration), and markedly reduced Fe_2O_3 for both samples. Na_2O increased in B1 (consistent with interlayer Na^+ retention) while K_2O decreased in B2. These compositional shifts confirm that the decantation–acid treatment sequence preferentially concentrates phyllosilicates while removing accessory minerals (quartz, calcite, pyrite) and soluble impurities.

Table 1. Chemical composition of enriched bentonites (wt%)

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	SO_3	L.O.I.
OB1	56.6	18.2	0.3	0.1	1.1	1.3	3.9	1.6	0.6	16.0
OB2	56.6	18.6	0.4	0.1	3.8	3.1	1.3	0.5	0.6	14.8

3.2. Particle Size Distribution After Enrichment

Enrichment substantially altered the granulometric profile of both bentonites. The coarse fraction (≥100 μm) decreased markedly due to sand removal during decantation, while the 5–1 μm and sub-1 μm fractions increased (Table 2). For OB1, the <1 μm fraction rose from 8.2% (raw) to 15.8%, and for OB2 from 3.1% to 8.7%. The H_2SO_4 treatment further disaggregated clay packets, increasing the ultrafine fraction — a key factor in expanding accessible surface area for adsorption.

Table 2. Particle size distribution of enriched bentonites (%)

Sample	≥100 μm	100–50 μm	50–10 μm	10–5 μm	5–1 μm	<1 μm
OB1	21.1	11.1	8.5	12.2	31.3	15.8
OB2	27.6	13.2	8.1	10.3	32.1	8.7

3.3. Textural Properties of Enriched Bentonites

N_2 adsorption–desorption data revealed that enrichment raised the BET specific surface area (S_BET) of B1 from 56.3 to 77.3 m^2/g (+37%) and of B2 from 42.7 to 61.2 m^2/g (+43%). Simultaneously, the mean pore radius decreased (B1: 4.15 → 3.61 nm; B2: 4.48 → 3.98 nm) and total pore volume increased (B1: 0.190 → 0.221 cm^3/g; B2: 0.175 → 0.203 cm^3/g) (Table 3). These changes are consistent with the removal of pore-blocking impurities and the partial acid leaching of Al^{3+} and Fe^{3+} from edge sites, creating new mesoporosity. The enrichment thus produces materials with better-developed porous networks that are more conducive to adsorption.

Table 3. Textural parameters of enriched bentonites (N_2 adsorption)

Sample	S_BET (m^2/g)	R_mean (nm)	V_total (cm^3/g)
OB1	77.3	3.61	0.221
OB2	61.2	3.98	0.203

3.4. Structural Changes upon Metal (Hydr)oxide Modification

XRD patterns of the four modified composites (FB1, FB2, KB1, KB2) showed several notable changes relative to enriched precursors. For the FB series (Fe/Mg/Mn), new diffraction peaks at 2θ = 33°, 35.6°, and 41° indicated the formation of iron oxide phases — hematite (α-Fe_2O_3) and magnetite (Fe_3O_4). The d_{001} peak of montmorillonite shifted to higher angles and broadened, signifying decreased and heterogeneous interlayer spacing (d_{001} = 1.54 nm for FB1 vs. 1.48 nm for KB1), reflecting cation replacement and partial delamination. Peaks consistent with MnO_2 were detected at 33° and 40.8° for all composites.

For the KB series (Ca/Zn/Mn), quartz d_{100} and d_{101} peaks at 20.79° and 26.61° were more pronounced, and an additional peak attributed to cristobalite appeared at 21.79°. The decreased d_{001} intensity and peak broadening in both series indicate disorganized but expanded interlayer regions — a structural state favorable for surface complexation with polyvalent metal ions. The d-spacing sensitivity to the modification ion type and degree of hydration is well established for montmorillonite composites [10].

3.5. Textural Properties of Modified Composites

Metal oxide coating dramatically enhanced all textural parameters relative to enriched precursors. S_BET values increased to 120.6 (FB1), 95.5 (FB2), 146.1 (KB1), and 115.7 m^2/g (KB2) — gains of 89–139% relative to the raw B1 and B2 samples (Table 4). KB1 exhibited the highest surface area (146.1 m^2/g), smallest pore radius (3.008 nm), and largest total pore volume (0.354 cm^3/g), making it the most texturally developed material in this study. The decrease in pore radius upon modification is attributable to partial pore filling by precipitated oxide clusters, while the overall volume increase reflects generation of new micro-mesopore interfaces at the clay-oxide boundary.

Table 4. Textural parameters of modified bentonite composites

Sample	Coating	S_BET (m^2/g)	R_mean (nm)	V_total (cm^3/g)
FB1	Fe/Mg/Mn	120.6	3.282	0.332
FB2	Fe/Mg/Mn	95.5	3.618	0.305
KB1	Ca/Zn/Mn	146.1	3.008	0.354
KB2	Ca/Zn/Mn	115.7	3.317	0.325

3.6. Adsorption Kinetics of Cu^{2+} and PO_4^{3-}

Equilibrium for Cu^{2+} adsorption was reached within 1 h for KB1, 4 h for FB1, and approximately 48–50 h for OB1 (enriched, unmodified). This kinetic acceleration in modified composites is mechanistically significant: in unmodified bentonite, Cu^{2+} uptake proceeds by interlayer cation exchange, which requires diffusion through the swelling, hydrating clay matrix — a slow process. In metal oxide-coated composites, adsorption occurs primarily through surface complexation at Fe/Mn/Zn oxyhydroxide sites, which are kinetically rapid and do not require lattice expansion [11]. This is

confirmed by the observation that Na^+ and K^+ — ions incapable of forming stable surface complexes — are not adsorbed by Fe-modified bentonites.

For PO_4^{3-}, equilibrium was achieved in ~3.5 h (FB1) and ~1 h (KB2), both substantially faster than unmodified forms. The anion adsorption mechanism involves ligand exchange at surface hydroxyl groups on oxide coatings — a well-established pathway for phosphate capture by iron oxyhydroxides [12].

3.7. Adsorption Isotherms and Capacity

Equilibrium data for Cu^{2+} adsorption were well described by the Langmuir model over the concentration range tested ($r^2 > 0.97$). Maximum adsorption capacities (Q_max) are summarized in Table 5. Modified composites substantially outperformed unmodified enriched bentonites. FB1 achieved the highest Cu^{2+} uptake (128.5 mg/g) and PO_4^{3-} uptake (153.3 mg/g). The adsorption sequence for phosphate followed: FB2 > FB1 > KB2 > KB1 > OB1 > OB2, which mirrors the ranking of specific surface area and micropore accessibility — confirming that texture drives anion adsorption capacity.

The significantly higher PO_4^{3-} capacity of FB composites relative to KB composites (~25% advantage) is attributed to the higher density of Fe–OH surface sites, which have a well-documented high affinity for phosphate via binuclear bidentate surface complexes [13]. In contrast, Zn^{2+} and Ca^{2+}-based coatings (KB series) contribute fewer anion-binding sites but more cation-exchange capacity — explaining their superior performance for water vapor adsorption (see Section 3.9).

Table 5. Maximum adsorption capacities (mg/g) for Cu^{2+} and PO_4^{3-} at pH 7, 25°C

Adsorbate	OB1	OB2	FB1	FB2	KB1	KB2
Cu^{2+}	108.3	96.2	128.5	112.1	123.4	106.5
PO_4^{3-}	74.8	69.5	153.3	120.4	144.9	109.2

3.8. pH Dependence of Adsorption

The effect of pH on Cu^{2+} adsorption followed the expected amphoteric pattern for metal oxide-coated aluminosilicates. As pH increased from 2 to 9, Cu^{2+} uptake increased for all sorbents: by 2.5 mg/g for OB1, 8.7 mg/g for FB1, and 11.1 mg/g for KB1 per pH unit increment from 7 to 9. This trend arises because at alkaline pH the clay edge sites and oxide surface become predominantly negatively charged (above the point of zero charge, PZC), attracting Cu^{2+} electrostatically in addition to specific complexation.

Phosphate adsorption exhibited inverse pH dependence: uptake declined as pH increased from 2 to 9. At pH 2, PO_4^{3-} adsorption on FB1 reached 61.2 mg/g; at pH 9, it fell to 49.1 mg/g (Table 6). This is consistent with the conversion of $Fe–OH_2^+$ sites (abundant at low pH, positively charged) to Fe–OH (neutral) and $Fe–O^-$ (negatively charged at high pH), reducing electrostatic affinity for anions. The optimal adsorption window for both ions — pH 2–10 — defines the operational envelope for practical application. Beyond this range, structural degradation of the composite may occur through competitive protonation or hydroxide precipitation reactions.

Table 6. pH-dependent adsorption capacities (mg/g) for Cu^{2+} and PO_4^{3-}

Adsorbate / pH	OB1	OB2	FB1	FB2	KB1	KB2
Cu^{2+} at pH=2	8	11	25	21	30	29
Cu^{2+} at pH=9	111	95	128	108.9	139	107.6
PO_4^{3-} at pH=2	19	12	61.2	60.1	59.2	58.2
PO_4^{3-} at pH=9	12	9	49.1	45.1	37.1	34.3

3.9. Vapor Adsorption: Water and Benzene

Adsorption isotherms of water vapor on all samples were classified as Type II (IUPAC), typical of predominantly mesoporous, hydrophilic materials. Three distinct regions were identified: rapid initial

uptake ($P/P_0 < 0.4$), a quasi-linear plateau ($P/P_0 = 0.4–0.8$), and a sharp rise toward saturation ($P/P_0 > 0.8$) indicative of multilayer condensation in mesopores. BET analysis of water vapor isotherms yielded S_BET values of 158.4 m^2/g (KB1) and 167.2 m^2/g (KB2), exceeding N_2-derived values — suggesting that water molecules probe additional interlayer micropore space inaccessible to N_2 at 77 K.

KB composites showed substantially higher water vapor uptake (monolayer capacity $A\infty = 2.44–2.57$ mol/kg) compared to FB composites ($A\infty = 1.53–2.11$ mol/kg) and unmodified enriched bentonites ($A\infty = 0.86–0.93$ mol/kg). This is attributed to the hydrophilic nature of $Ca^{2+}/Zn^{2+}/Mn^{2+}$ oxide surfaces, which present abundant polar hydroxyl groups favorable for water molecule interaction.

In contrast, benzene vapor isotherms (Type L, well-fitted by the Langmuir model) favored FB composites: $A\infty(FB2) = 0.569$ mol/kg > $A\infty(KB2) = 0.513$ mol/kg > $A\infty(FB1) = 0.465$ mol/kg > $A\infty(KB1) = 0.402$ mol/kg. The proposed mechanism for benzene adsorption involves π-complexation between the aromatic ring and Fe^{3+} Lewis acid sites — analogous to π-back donation observed in zeolite-metal ion systems [14]. This dual hydrophilic (KB)/hydrophobic (FB) selectivity suggests that the two coating chemistries can be deployed for complementary applications: KB for gas drying and polar VOC removal; FB for nonpolar organic capture and catalytic oxidation.

Table 7. Textural and adsorption parameters from water vapor and benzene vapor isotherms

Sample	A∞ H_2O (mol/kg)	S H_2O (m^2/g)	ΣV H_2O (cm^3/g)	A∞ C_6H_6 (mol/kg)	S C_6H_6 (m^2/g)	ΣV C_6H_6 (cm^3/g)
OB1	0.925	60.1	0.072	0.213	51.3	0.060
KB1	2.436	158.4	0.131	0.402	99.5	0.099
FB1	2.111	137.2	0.140	0.465	108.8	0.100
OB2	0.861	56.0	0.075	0.197	47.4	0.066
KB2	2.569	167.2	0.141	0.513	123.2	0.130
FB2	1.534	101.1	0.111	0.569	136.2	0.129

3.10. Sorption and Catalytic Oxidation of Petroleum Contaminants

Kinetic profiles for petroleum product removal showed distinct patterns for enriched versus modified bentonites. For OB1 and OB2, maximum reduction (~60%) was achieved within the first 20 min via physical adsorption, after which the curves plateaued — consistent with saturation of accessible hydrophobic surface sites. Modified composites (FB, KB series) displayed a two-stage kinetic profile: a rapid initial drop within the first 5 min (likely surface adsorption), followed by a secondary decrease around 30 min (attributed to diffusion of larger organic molecules into mesopores and intercalation into expanded interlayers).

All four modified composites reduced petroleum concentrations by >80% via adsorption alone. However, fat removal was more selective: KB1 and KB2 removed only 62–66% of oils, suggesting that the hydrophilic Ca/Zn/Mn oxide surface resists lipid accumulation. When H_2O_2 was introduced (360 mg/L) at T > 20 °C, FB1 and FB2 achieved ~99% oxidative removal of both petroleum products and fats within 20–25 min — a performance attributable to Fenton-like generation of hydroxyl radicals by surface Fe^{3+}/Fe^{2+} redox cycling [12]. KB1 and KB2 reached ~80% oxidation, reflecting the lower Fe content of these composites.

The catalytic advantage of Fe-modified bentonites for heterogeneous Fenton-like reactions is consistent with literature reports on iron oxide pillared clays and Fe-PILC catalysts [15]. The present materials benefit from the synergistic combination of high surface area, thermal stability (no swelling after 300 °C calcination), and accessible redox-active iron sites. Based on these results, FB1 was recommended for industrial pilot testing at the Mubarek Gas Processing Plant (Uzbekistan) for treatment of petroleum-containing effluents, and KB1 for natural gas drying applications.

4. ENVIRONMENTAL SIGNIFICANCE AND PRACTICAL IMPLICATIONS

The results of this study demonstrate that both the starting clay type (Na vs. Ca/Mg) and the coating chemistry (Fe/Mg/Mn vs. Ca/Zn/Mn) critically determine the functional properties of the resulting composite. Na-bentonite (B1) consistently outperformed Ca/Mg-bentonite (B2) in most adsorption metrics — a consequence of its higher initial CEC, finer original particle size distribution, and greater swellability, which facilitate more uniform oxide coating formation. The performance advantage of KB1 over KB2 and FB1 over FB2 reinforces this conclusion.

From an ecological engineering perspective, these composites present several advantages over conventional treatment materials: (i) raw materials are locally abundant and low-cost; (II) the synthesis avoids toxic organic modifiers (unlike organobentonites); (IIi) the dual adsorption–catalytic function reduces treatment steps and reagent consumption; (iv) the stabilized composite structure minimizes secondary contamination by modifier leaching (confirmed by chemical stability testing); and (v) the materials are pH-resilient across the 2–10 range relevant to most industrial effluents.

Comparison with published modified bentonite adsorbents (Table 8) shows that the Q_max values obtained in this work (128.5 mg/g Cu^{2+}; 153.3 mg/g PO_4^{3-}) are competitive with or superior to reported Fe-pillared clay and iron-oxide-coated clay materials, particularly at neutral pH. The simultaneous multi-contaminant capacity (heavy metals + phosphates + petroleum + lipids) within a single material class represents a significant practical advantage for integrated wastewater treatment scenarios encountered in mining, agricultural processing, and petroleum refining effluents.

Table 8. Comparison of Cu^{2+} and PO_4^{3-} adsorption on modified bentonites from recent literature

Material	Q_max Cu^{2+} (mg/g)	Q_max PO_4^{3-} (mg/g)	pH	Reference
Fe-PILC bentonite	85–100	90–120	6–7	[10]
Fe_2O_3-coated montmorillonite	95–118	110–140	5–7	[11]
Acid-activated bentonite	60–80	50–70	6	[7]
This study (FB1)	128.5	153.3	7	Present work
This study (KB1)	123.4	144.9	7	Present work

5. CONCLUSIONS

This study systematically characterized the structural and functional evolution of two Uzbekistan bentonite clays (Na-type B1 and Ca/Mg-type B2) through sequential enrichment and metal (hydr)oxide modification. The key findings are:

1. H_2SO_4-assisted decantation enrichment increased montmorillonite content, BET surface area (by 37–43%), and fine particle fraction while removing quartz and accessory minerals.
2. Modification at pH 9–11 with $Fe^{3+}/Mg^{2+}/Mn^{2+}$ or $Ca^{2+}/Zn^{2+}/Mn^{2+}$ salt mixtures, followed by 300 °C thermal stabilization, created composite materials with S_BET up to 146 m^2/g and V_total up to 0.354 cm^3/g — the highest values for metal oxide-coated bentonites from this region.
3. Fe/Mg/Mn-modified composites (FB series) maximized Cu^{2+} (128.5 mg/g) and PO_4^{3-} (153.3 mg/g) adsorption via surface complexation, were selective for benzene vapor over water, and catalytically oxidized 99% of petroleum/fat contaminants with H_2O_2 in <25 min via Fenton-like chemistry.
4. Ca/Zn/Mn-modified composites (KB series) displayed higher water vapor uptake (167 m^2/g water-BET surface), making them suitable for gas drying applications.
5. Na-bentonite (B1)-based composites consistently outperformed Ca/Mg-bentonite (B2) composites, attributed to superior initial CEC and textural properties.
6. The operational pH window of 2–10 and kinetic equilibration within 1–4 h for modified materials confirms their practical viability for engineering-scale applications.

These results establish Fe/Mg/Mn and Ca/Zn/Mn oxide-coated bentonites as multifunctional, low-cost materials for integrated treatment of complex wastewater streams. Future work should address regeneration cycles, column flow performance, and life-cycle assessment to support scale-up decisions.

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