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THERMOCHEMICAL ACTIVATION OF LOCAL NAVBAHOR BENTONITE FOR THE COMBINED COAGULATION–FLOCCULATION–ADSORPTION TREATMENT OF PETROLEUM REFINERY WASTEWATER

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Abstract. Petroleum-refinery wastewater is a complex effluent containing oil products, heavy-metal ions, chloride and ammonium species that require multi-stage treatment prior to discharge or reuse. This study reports the development of a low-cost adsorbent from local Navbahor (Navoiy region, Uzbekistan) montmorillonite-rich bentonite through thermal, chemical (HNO_3) and combined thermochemical activation, and its application – together with coagulation and flocculation–to the treatment of real effluent from the Bukhara Oil Refinery. Systematic single-factor experiments (100-1000°C; HNO_3 3-30 wt.%) showed that thermal treatment alone raised the BET surface area from 95 to a maximum of 193 m^2/g at 500 °C, while acid treatment alone raised it to 214 m^2/g at 20% HNO3; beyond these levels dehydroxylation and partial framework collapse reduced performance. Combining 20% HNO_3 activation with subsequent calcination at 500°C produced the most effective adsorbent (MB), with a BET surface area of 284 m^2/g (+199%), total pore volume of 0.438 cm^3/g (+271%) and cation-exchange capacity of 118 mEq/100 g (+34%), confirmed by FTIR, EDXRF and DTA/TG analysis. Batch adsorption data fitted the Langmuir model well (R^2 = 0.980-0.995), giving maximum capacities for MB of 136.8, 107.2, 59.5 and 150.3 mg/g for oil products, Fe^{3+}, Cl^- and NH^{4+}, respectively – 2.8 to 3.9 times higher than for the unmodified clay. A three-stage combined treatment ($Al_2(SO_4)_3$ coagulation, sodium carboxymethylcellulose flocculation, MB adsorption) applied to actual refinery wastewater achieved removal efficiencies of 97.8% (oil products), 95.4% (Fe), 97.1% (suspended solids), 91.2% (NH^{4+}), 88.3% (COD), 78.6% (Cl^-) and 74.5% (total dissolved solids) under optimized conditions (100 mg/L coagulant, 2.5 mg/L flocculant, 5 g/L adsorbent, pH 6.0-7.0, 120 min contact time), bringing all parameters below the regulatory discharge limits. The results demonstrate that thermochemically modified local bentonite is a technically viable and economical substitute for imported adsorbents in petroleum-industry wastewater treatment.

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Keywords: bentonite; thermochemical activation; adsorption isotherm; petroleum refinery wastewater; coagulation-flocculation; Langmuir model.

Аннотация. Сточные воды нефтеперерабатывающих заводов представляют собой сложные сточные воды, содержащие нефтепродукты, ионы тяжелых металлов, хлориды и аммоний, которые требуют многоступенчатой очистки перед сбросом или повторным использованием. В этом исследовании сообщается о разработке недорогого адсорбента из местного бентонита, обогащенного монтмориллонитом, из Навбахора (Навоийская область, Узбекистан) путем термической, химической (HNO3) и комбинированной термохимической активации, и его применении - вместе с коагуляцией и флокуляцией - для очистки реальных сточных вод Бухарского нефтеперерабатывающего завода. Систематические однофакторные эксперименты (100-1000°C; HNO3 3-30 мас.%) показали, что только термическая обработка увеличивала площадь поверхности BET с 95 до максимальной 193 м2/г при 500°C, в то время как только кислотная обработка увеличивала ее до 214 м2/г при 20% HNO3; при превышении этих уровней дегидроксилирование и частичное разрушение каркаса снижали производительность. Сочетание 20%-ной активации HNO3 с последующим прокаливанием при 500°C позволило получить наиболее эффективный адсорбент (MB) с площадью поверхности BET 284 м2/г (+199%), общим объемом пор 0,438 см3/г (+271%) и катионообменной способностью 118 мэкв/100 g (+34%), что подтверждено результатами ИК-спектроскопии, EDXRF-анализа и DTA/TG-анализа. Данные по периодической адсорбции хорошо соответствовали модели Ленгмюра (R2 = 0,980-0,995), что дает максимальную производительность по MB в 136,8, 107,2, 59,5 и 150,3 мг/г для нефтепродуктов, Fe3+, Cl^- и NH4+ соответственно, что в 2,8–3,9 раза выше, чем для немодифицированной глины. Трехступенчатая комбинированная очистка (коагуляция Al2(SO4)3, флокуляция карбоксиметилцеллюлозы натрия, адсорбция MB) сточных вод нефтеперерабатывающего завода позволила достичь эффективности удаления 97,8% (нефтепродуктов), 95,4% (железа), 97,1% (взвешенных веществ), 91,2% (NH4+), 88,3% (ХПК), 78,6% (Cl^-) и 74,5% (общее количество растворенных твердых веществ) при оптимальных условиях (100 мг/л коагулянта, 2,5 мг/л флокулянта, 5 г/л адсорбента, pH 6,0-7,0, время контакта 120 мин), что позволяет снизить все параметры до нормативных пределов расхода. Результаты показывают, что термохимически модифицированный местный бентонит является

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технически целесообразной и экономичной заменой импортных адсорбентов для очистки сточных вод нефтяной промышленности.

Ключевые слова: бентонит; термохимическая активация; изотерма адсорбции; сточные воды нефтеперерабатывающих заводов; коагуляция-флокуляция; модель Ленгмюра.

Annotatsiya. Neftni qayta ishlash zavodining oqava suvlari neft mahsulotlari, og'ir metallar ionlari, xlorid va ammoniy turlarini o'z ichiga olgan murakkab oqava suv bo'lib, ular oqizishdan oldin yoki qayta ishlatishdan oldin ko'p bosqichli tozalashni talab qiladi. Ushbu tadqiqot mahalliy Navbahor (Navoiy viloyati, O'zbekiston) montmorillonitga boy bentonitdan termal, kimyoviy (HNO3) va kombinatsiyalangan termokimyoviy aktivatsiya orqali arzon narxlardagi adsorbentni ishlab chiqish va uni koagulyatsiya va flokulyatsiya bilan birgalikda Buxoro neftni qayta ishlash zavodidan haqiqiy oqava suvlarni tozalash uchun qo'llash haqida xabar beradi. Tizimli bir omilli tajribalar (100-1000°C; HNO3 3-30 Vt.%) kislota davolash yolg'iz 95% HNO193 da 2 M500/g uni ko'tardi esa issiqlik davolash yolg'iz, 514 m2/g maksimal 3 dan BET yuzasi maydoni ko'tardi ko'rsatdi; bu darajadagi dehidroksillanish va qisman kesish buzish tushgan ishlash orqasida. 20% HNO3 aktivatsiyasini 500% da keyingi kalsinatsiya bilan birlashtirib, BET yuzasi 284 m2/g (+199%), umumiy teshik hajmi 0,438 sm3/g (+271%) va kation almashinuvi quvvati 118 mEq / 100 bo'lgan eng samarali adsorbent (MB) ishlab chiqarildi. ftir, EDXRF va DTA/TG tahlillari tomonidan tasdiqlangan g (+34%). Ommaviy adsorbsion ma'lumotlar Langmuir modelini yaxshi jihozladi (R2 = 0.980-0.995), neft mahsulotlari uchun 136.8, 107.2, 59.5 va 150.3 mg/g MB uchun maksimal quvvat, Fe3 va Cl^- va NH4+ uchun mos ravishda – o'zgartirilmagan loyga nisbatan 2.8 dan 3.9 baravar yuqori. A uch bosqichli Birlashgan davolash (Al2(SO4)3 ivish, natriy karboksimetilsellyuloza flokulation, MB yutish) 97,8% (neft mahsulotlari), 95,4% (Fe), 97,1% (to'xtatib qattiq), 91,2% (NH4+), 88,3% (haqiqiy qayta ishlash zavodi chiqindi suv erishilgan ko'chirish samaradorligi amaliy (Cod), 78,6% (Cl^-) va 74,5% (jami erigan qattiq moddalar) optimallashtirilgan sharoitlarda (100 mg/l koagulyant, 2,5 mg/L flokulyant, 5 g/L adsorbent, pH 6.0-7.0, 120 min aloqa vaqti), barcha parametrlarni tartibga solish razryad chegaralaridan pastga olib keladi. Natijalar shuni ko'rsatadiki, termokimyoviy modifikatsiyalangan mahalliy bentonit neft sanoati chiqindi suvlarini tozalashda import qilinadigan adsorbentlarning texnik jihatdan foydali va iqtisodiy o'rnini bosuvchi hisoblanadi.

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Kalit so'zlar: bentonit; termokimyoviy faollashuv; adsorbsiya izotermi; neftni qayta ishlash zavodining oqava suvlari; koagulyatsiya-flokulyatsiya; Langmyur modeli.

1. INTRODUCTION.

Protection of water bodies from industrial effluents is among the most pressing environmental problems worldwide, and it is particularly acute for large process industries such as petroleum refining, petrochemistry, textile manufacturing and mining/metallurgy, whose wastewater has a complex and highly variable composition [1-3]. Refinery effluents typically contain free and emulsified oil products, suspended solids, heavy-metal ions (mainly Fe^{2+}/Fe^{3+}), chlorides, ammonium nitrogen and a high chemical oxygen demand (COD), so that a single treatment step is rarely sufficient to meet discharge standards [4,5]. Consequently, the development of complex, energy- and resource-saving treatment schemes that combine coagulation, flocculation and adsorption is of considerable scientific and practical interest.

Among the wide variety of adsorbents used for wastewater purification, natural clay minerals – and bentonite in particular – are attractive because of their wide availability, low cost, high specific surface area, well-developed layered structure and pronounced cation-exchange capacity [6-8]. The adsorption and structural properties of bentonites, as well as approaches to their activation and modification, have been studied extensively by Ozcan, Al-Khalaf, Marey, Zaki, Guo, Unuabonah, Pollard, Usman, Ekwueme, Alaje, Wang, Kormosh and other researchers abroad, and by Akhmedov, Narmetova, Aripov, Turabdjanov, Ikhtiyarova, Umarov, Narzullaeva, Abduraximov, Salikhanova, Eshmetov, Jumayeva and Adizov in Uzbekistan [6-19]. Acid activation (mainly with H2SO4, HCl or HNO_3), thermal (calcination) activation and combined thermochemical treatment are the most common ways of enhancing the specific surface area, pore volume and number of active adsorption sites of raw bentonite [9,10,20-24]. Acid leaching removes exchangeable Ca^{2+}, Mg^{2+} and Na^{+} cations and partially dealuminates the octahedral sheet, opening the interlayer space and developing mesoporosity, while subsequent calcination removes structural water and consolidates the newly formed pore network [20-23,25].

Despite this substantial body of work, two gaps remain. First, the colloid-chemical and textural properties of the alkaline-earth (Ca-Mg) bentonite of the Navbahor deposit (Navoiy region, Uzbekistan) – a large and, so far, only partially studied local raw-material base – have not been systematically compared with imported analogues, nor has a combined thermochemical activation protocol been

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optimized for this specific clay. Second, most published studies address the removal of a single contaminant class (oil, a given metal ion, or a dye) by a modified bentonite in synthetic solution, whereas real refinery wastewater simultaneously carries oil products, Fe, Cl^-, NH^{4+}, suspended solids and a high COD; a combined coagulation-flocculation-adsorption scheme using a single locally produced modified adsorbent has rarely been reported for such multicomponent effluents [26-31].

The aim of the present work was therefore to develop a technology for producing an efficient adsorbent from local Navbahor bentonite by thermal, chemical and thermochemical modification, and to use this adsorbent – in combination with a coagulant and a flocculant – for the complex treatment of real petroleum-refinery wastewater. The specific objectives were: (i) to characterize the colloid-chemical and textural properties of natural Navbahor bentonite in comparison with other local and foreign clays; (ii) to establish, through single-factor experiments, the optimum conditions of thermal (100-1000°C), chemical (HNO_3, 3-30%) and combined thermochemical modification; (iii) to characterize the resulting adsorbent by FTIR, DTA/TG and EDXRF; (iv) to quantify, through batch experiments and Langmuir/Freundlich isotherm modelling, the adsorption capacity of the modified bentonite towards oil products, Fe^{3+}, Cl^- and NH^{4+}; and (v) to determine the optimum parameters of a combined coagulation-flocculation-adsorption process for real wastewater from the Bukhara Oil Refinery and to compare the resulting effluent quality with regulatory discharge limits.

2. MATERIALS AND METHODS.

2.1. Materials

Natural bentonite clay from the Navbahor deposit (Navoiy region, Republic of Uzbekistan) was used as the raw material. For comparison, samples of Gumbria (Georgia), Kattakurgan, Shorsu, Tamdi-Tau and Cherkassy (Ukraine) bentonites/palygorskite, as well as Tulsakh alkaline-earth bentonite (Fergana region), were used as reference materials. Analytical-grade nitric acid (HNO3, 65%), aluminium sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ (coagulant), sodium salt of carboxymethyl cellulose (Na-CMC, flocculant) and polyacrylamide (PAA) were used as received. The wastewater under study was sampled from the water-and-sewage (VIK) unit of the ‘Bukhara Oil Refinery’ LLC.

2.2. Preparation of thermally, chemically and thermochemically modified bentonite

Raw bentonite was crushed to a particle size below 0.08 mm, dried at 120°C for 5 h, dispersed in distilled water (1:10, w/v) and left to sediment for 24 h at room temperature; the finest (colloidal) fraction was separated by centrifugation (3000 rpm, 5 min), air-dried for 12 h and oven-dried at 75°C for 4 h. For thermal

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modification, this fraction was calcined in a muffle furnace at temperatures from 100 to 1000°C (step 100°C) for 1-2 h. For chemical modification, the clay was treated with HNO_3 solutions of 3, 5, 10, 15, 20, 25 and 30 wt.% (solid:liquid = 1:3.5) at 80-90°C for 3 h under stirring, then washed repeatedly with distilled water until pH 6.0-6.5 and dried at 65°C for 12 h. For thermochemical (combined) modification, the sample was first activated with 15-20% HNO_3 as above and then calcined at 300, 500 or 700°C for 1-2 h. On the basis of these experiments, the sample obtained with 20% HNO_3 followed by calcination at 500°C was selected as the optimum modified bentonite (denoted MB below); the untreated clay is denoted TB (natural bentonite).

2.3. Characterization methods

The textural properties (specific surface area SBET, total pore volume, pore-size distribution) were determined by low-temperature N_2 adsorption-desorption at 77 K over the relative pressure range 0.05-0.99 on an ASAP-2400 analyser, with the specific surface calculated by the Brunauer-Emmett-Teller (BET) method and the mesopore-size distribution by the Barrett-Joyner-Halenda (BJH) method [32,33]. The granulometric composition was determined by sedimentation analysis (Sabanin-Robinson method) [34]; the swelling of the clays in water at 45°C, the wetting heat and the cation-exchange capacity (CEC, ammonium acetate method) were determined by standard colloid-chemical procedures [34,35]. Functional groups were analysed by Fourier-transform infrared spectroscopy (FTIR) over the range 4000-400 cm^{-1}. Thermal behaviour was studied by derivatography (simultaneous TG/DTG/DTA) on a Shimadzu DTG/DTA instrument under a controlled heating rate in air. Elemental and oxide composition were determined by energy-dispersive X-ray fluorescence spectroscopy (EDXRF) on a Rigaku NEX DE spectrometer operated in air in two measurement modes for a total counting time of 200 s.

2.4. Wastewater sampling and analytical methods

The quality of the raw and treated wastewater was assessed by standard methods used at the analytical laboratory of the refinery and in the present study: pH was measured potentiometrically with a glass electrode (interstate standard GOST ISO 10523-2017, equivalent to ISO 10523:2008); oil-product content was determined by the gravimetric method (Uz DSt 0697:2015, Uz DSt 0791:2019); suspended solids were determined gravimetrically after filtration through a 0.45 μm membrane and drying at 105 °C; total iron was determined photometrically with sulfosalicylic acid (GOST 4011-72, Uz DSt 0706:2016) at 400-430 nm; chloride ion was determined by argentometric titration with $AgNO_3$ (RD 52.24.407-2006); total dissolved solids (dry residue) were determined gravimetrically after evaporation and drying at 105-110°C (GOST 18164-72); and

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ammonium ion/ammonium nitrogen were determined photometrically after colour development with Nessler's reagent (GOST 23268.10-78). Chemical oxygen demand (COD) was determined by the standard dichromate method.

2.5. Batch adsorption experiments and isotherm modelling

Batch adsorption isotherms were obtained for four target contaminants using both the natural (TB) and the optimum thermochemically modified (MB) bentonite. Oil-product adsorption was studied using a model diesel-fuel/water emulsion (C_0 = 2-100 mg/L) at T = 25 ± 1°C, pH 6.8 ± 0.2, adsorbent dose m = 5 g/L, stirring at 180 rpm, contact time 120 min; the residual oil-product concentration was measured by IR spectroscopy (λ = 3420 nm) after CCl_4 extraction. Fe^{3+} adsorption was studied with a $FeCl_3$ solution (C_0 = 1-100 mg/L) at pH 4.5 (to avoid hydroxide precipitation), m = 3 g/L, contact time 90 min; residual Fe^{3+} was measured by atomic absorption spectroscopy (AAS). Cl^- adsorption was studied with a NaCl solution (C_0 = 10-500 mg/L) at pH 7.0, m = 5 g/L, contact time 60 min; residual Cl^- was measured by argentometric titration. NH^{4+} adsorption was studied with an NH_4Cl solution (C_0 = 5-350 mg/L) at pH 7.0, m = 3 g/L, contact time 120 min; residual NH^{4+} was measured photometrically with Nessler's reagent. Equilibrium data were fitted to the Langmuir ($q_e = q_m K L C_e / (1+KLC_e)$) and Freundlich ($q_e = KFC_e 1/n$) isotherm models by linear regression; the corresponding linear forms $C_e/q_e = f(C_e)$ and $\log q_e = \log KF + (1/n)\cdot \log C_e$ were used to obtain qm, KL, KF, 1/n and the coefficient of determination R^2 for each system.

2.6. Combined coagulation-flocculation-adsorption treatment

The combined treatment of real refinery wastewater was carried out in three consecutive stages: (i) coagulation with $Al_2(SO_4)_3 \cdot 18H_2O$ at 20-140 mg/L; (ii) flocculation with Na-CMC at 0.5-3.5 mg/L (with PAA and $Ca(OH)_2$ (3-5 mL of a 10% solution) used to intensify floc settling); and (iii) adsorption with the thermochemically modified bentonite (MB, particle size 0.2-0.4 μm) at adsorbent doses and contact times optimized in preliminary experiments. Jar-test experiments were performed at T = 25°C over the pH range 5.0-9.0, with settling for 10-15 min prior to sampling of the supernatant for analysis. Colour and turbidity were monitored with a FEK-LF-72M photoelectric colorimeter using a 10 mm standard cuvette and distilled water as the reference.

2.7. Pilot-scale trial and technical-economic evaluation

In addition to the laboratory-scale jar tests, a two-stage pilot trial was carried out directly at the physico-chemical treatment unit of the Bukhara Oil Refinery, in cooperation with the plant's ecology laboratory, to compare the developed MB-based technology with the aluminium-sulphate/polyacrylamide technology currently used on site under identical raw-wastewater conditions. Reagent doses (including an auxiliary $Ca(OH)_2$ addition to promote floc settling) were first tested

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at an initial level and then adjusted in a second trial to avoid excessive alkalization of the treated water. A preliminary technical-economic evaluation of an industrial-scale production line for the modified bentonite was subsequently performed using standard capital-budgeting indicators (total investment, annual production cost, unit production cost, selling price at a fixed profit margin, annual revenue, net economic effect relative to import substitution, and simple payback period), based on the material and energy balances of the designed process.

3. RESULTS AND DISCUSSION.

3.1. Colloid-chemical characterization of natural Navbahor bentonite

Sedimentation analysis (Sabanin-Robinson method, Table 1) showed that all investigated clays belong to a finely dispersed raw-material class dominated by particles of 1.0-10 μm; the alkaline-earth bentonites contain a larger proportion of the finest (<0.01 mm) fraction than the Cherkassy palygorskite reference, confirming their comparatively lower mechanical strength.

Table 1.

Particle-size distribution of local and foreign natural bentonites

Deposit / clay type	<0.01 mm, %	<0.1 mm, %	<1.0 mm, %
Cherkassy palygorskite (Ukraine, reference)	65.1	31.3	3.6
Tulsakh alkaline-earth bentonite (Fergana region)	71.3	26.0	2.7
Navbahor carbonate alkaline-earth bentonite (Navoiy region)	76.5	21.4	2.1

The specific surface area of the natural Navbahor carbonate alkaline-earth bentonite (286 m^2/g, Table 2) is comparable with, and in some cases exceeds, that of well-known foreign analogues such as the Cherkassy (295 m^2/g) and Gumbria (270 m^2/g) bentonites, indicating that the local raw material is a promising substitute for imported adsorbents even prior to modification.

Table 2.

Specific surface area of local and foreign natural bentonites

Deposit / clay type	Specific surface area, m^2/g
Gumbria bentonite (Georgia), reference	270
KattaqUrg'on bentonite	155
Shorsu bentonite	170

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Deposit / clay type	Specific surface area, m^2/g
Tamdi-Tau bentonite	195
Navbahor alkaline bentonite	105
Navbahor alkaline-earth bentonite	110
Cherkassy alkaline-earth bentonite, reference	295
Tulsakh alkaline-earth bentonite	273
Navbahor carbonate alkaline-earth bentonite	286

Chemical analysis (Table 3) confirmed that both the alkaline (AB) and alkaline-earth (AEB) Navbahor bentonite fractions are dominated by SiO_2 and Al_2O_3, consistent with a montmorillonite-based aluminosilicate structure with a general formula $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$; the AEB fraction contains more SiO_2 (61.2%) but less Fe_2O_3 than the AB fraction, while both are relatively rich in exchangeable Ca, Mg and Na oxides, which strongly influence subsequent sorption and processing behaviour.

Table 3.

Chemical (oxide) composition of natural Navbahor bentonite fractions, wt.%

Deposit / clay type	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Other, %
Alkaline bentonite (AB)	57.91	13.69	5.10	1.84	0.48	1.53	1.75	17.7
Alkaline-earth bentonite (AEB)	61.2	15.9	2.3	3.1	3.2	1.1	0.6	12.6

Swelling and wetting-heat measurements (t = 45°C) showed a maximum water uptake of 1.22-1.40 cm^3/g and a wetting heat of 17.3-25.8 kcal/g across the samples studied, with the bound-water content ranging from 8 to 21% depending on clay type; these values, together with textural data obtained by low-temperature N_2 adsorption (SBET = 94.6-96.8 m^2/g, total adsorption volume 0.34-0.38 × 10^{-3} m^3/kg for the natural alkaline and alkaline-earth bentonite, respectively), were noticeably lower than those of standard industrial adsorbents ($S \geq 150$ m^2/g), which justified the subsequent modification study.

3.2. Effect of thermal activation on textural properties

Calcination of Navbahor bentonite over the range 100-1000°C (Table 4, Fig. 1) produced a characteristic bell-shaped dependence of SBET and pore volume on temperature. Below 500°C, progressive loss of physisorbed and interlayer water opens new mesopores and increases the specific surface area from 95 to a

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maximum of 193 m²/g (pore volume 0.264 cm³/g) at 500°C. Above 600°C, dehydroxylation of the montmorillonite lattice and the onset of structural collapse reduce the surface area; above 900°C, sintering causes pore closure and a sharp decline to 31 m²/g at 1000 °C. The optimum calcination temperature for Navbahor bentonite is therefore 400-500°C, consistent with the general behaviour reported for other smectite clays [20,21].

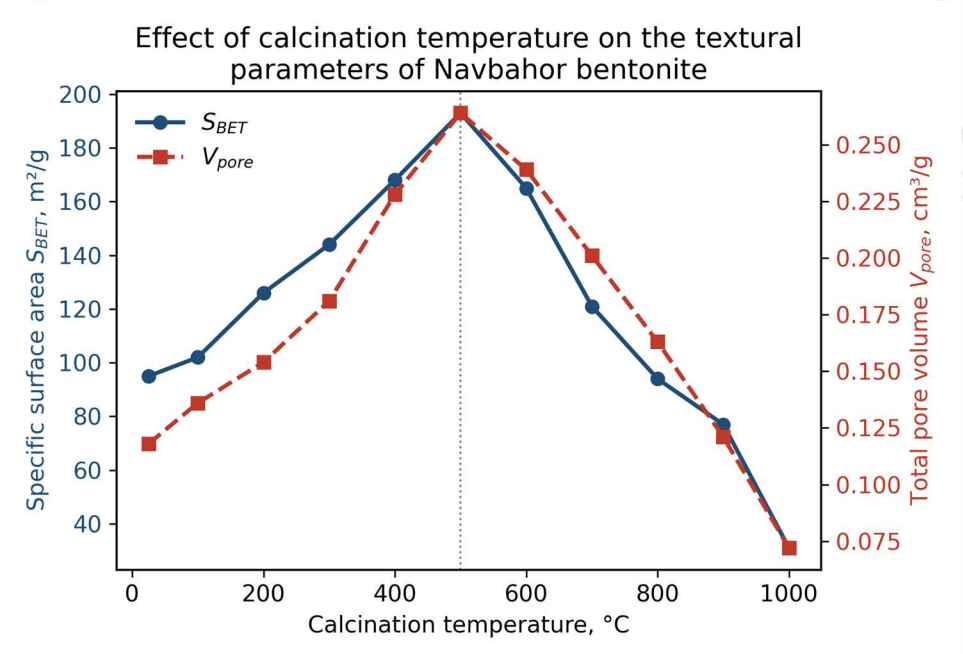


Fig. 1. Effect of calcination temperature on the specific surface area (SBET) and total pore volume of Navbahor bentonite.

Table 4.

Effect of calcination temperature on the textural properties of Navbahor bentonite

Calcination temperature, °C	S_{BET}, m²/g	Total pore volume, cm³/g	Structural state
Raw bentonite	95	0.118	Natural layered structure preserved
100	102	0.136	Onset of physisorbed water release
200	126	0.154	Partial interlayer water release
300	144	0.181	Mesopore development
400	168	0.228	Maximum surface activity

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Calcination temperature, °C	S_{BET}, m²/g	Total pore volume, cm³/g	Structural state
500	193	0.264	Optimal textural parameters
600	165	0.239	Onset of dehydroxylation
700	121	0.201	Partial collapse of crystal structure
800	94	0.163	Increasing amorphous-phase fraction
900	77	0.121	Partial pore closure (sintering onset)
1000	31	0.072	Sintering and structural degradation

3.3. Effect of chemical activation with HNO_3

Acid activation with HNO_3 (3-30%, Table 5, Fig. 2) removes exchangeable Ca^{2+}, Mg^{2+} and Na^{+} cations and partially dealuminates the octahedral sheet (Bentonite-Ca + $2HNO_3$ → Bentonite-2H + $Ca(NO_3)_2$), progressively opening the interlayer space. S_{BET} increased monotonically from 95 m²/g (raw) to a maximum of 214 m²/g at 20% HNO_3 (pore volume 0.347 cm³/g, mesopore fraction 85%). At 25-30% HNO_3, however, excessive acid attack caused partial collapse of the montmorillonite framework, closing some pores and reducing the surface area to 149-186 m²/g. The optimum HNO_3 concentration for chemical activation of Navbahor bentonite was therefore taken as 15-20%.

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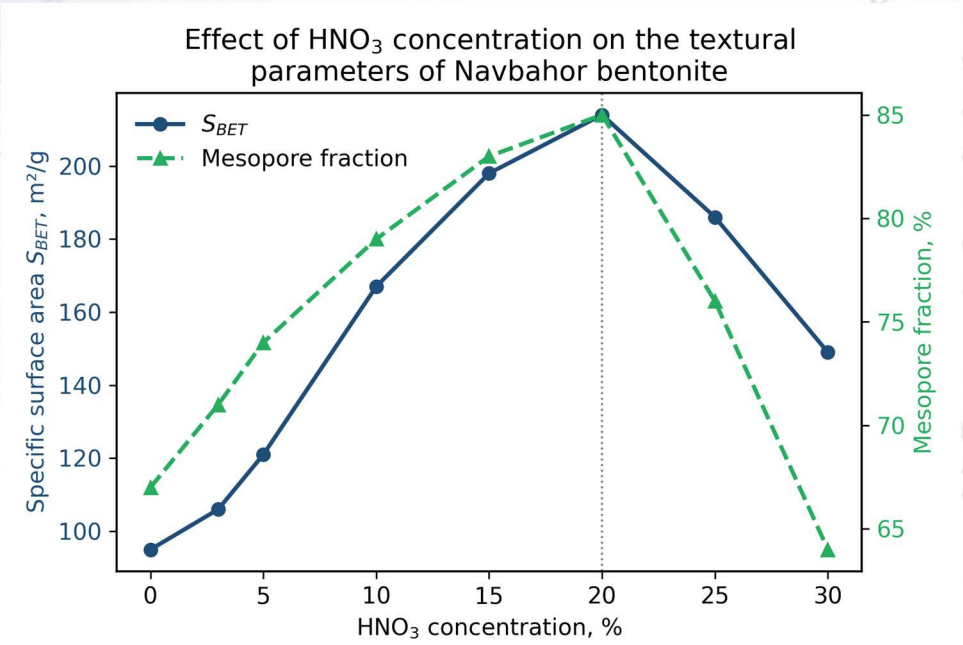


Fig. 2. Effect of HNO_3 concentration on the specific surface area and mesopore fraction of Navbahor bentonite

Table 5.

Effect of HNO_3 concentration on the textural properties of Navbahor bentonite

HNO_3 concentration, %	S_{BET}, m²/g	Total pore volume, cm³/g	Average pore diameter, nm	Mesopore fraction, %
0 (raw)	95	0.118	6.8	67
3	106	0.158	7.3	71
5	121	0.204	8.0	74
10	167	0.276	9.1	79
15	198	0.318	10.0	83
20	214	0.347	10.8	85
25	186	0.291	11.9	76
30	149	0.228	13.5	64

3.4. Thermochemical (combined) modification: optimum conditions

Combining chemical and thermal activation gave a markedly greater improvement in textural properties than either treatment alone (Table 6, Fig. 3). The sample activated with 20% HNO_3 and subsequently calcined at 500°C (denoted MB) exhibited the best overall performance: SBET = 284 m²/g (a 2.99-fold increase relative to raw bentonite), total pore volume = 0.438 cm³/g (3.71-fold increase) and a mesopore fraction of 91%. Complementary titration confirmed an

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increase in cation-exchange capacity from 88 to 118 mEq/100 g. These improvements are attributed to the synergistic combination of (i) an acid stage that removes octahedral Al^{3+}/Mg^{2+} and generates coordinatively unsaturated sites, and (ii) a thermal stage that removes structural water, opens new micro- and mesopores and strengthens the Si-O-Si framework, together widening the interlayer space available for ion exchange and molecular adsorption.

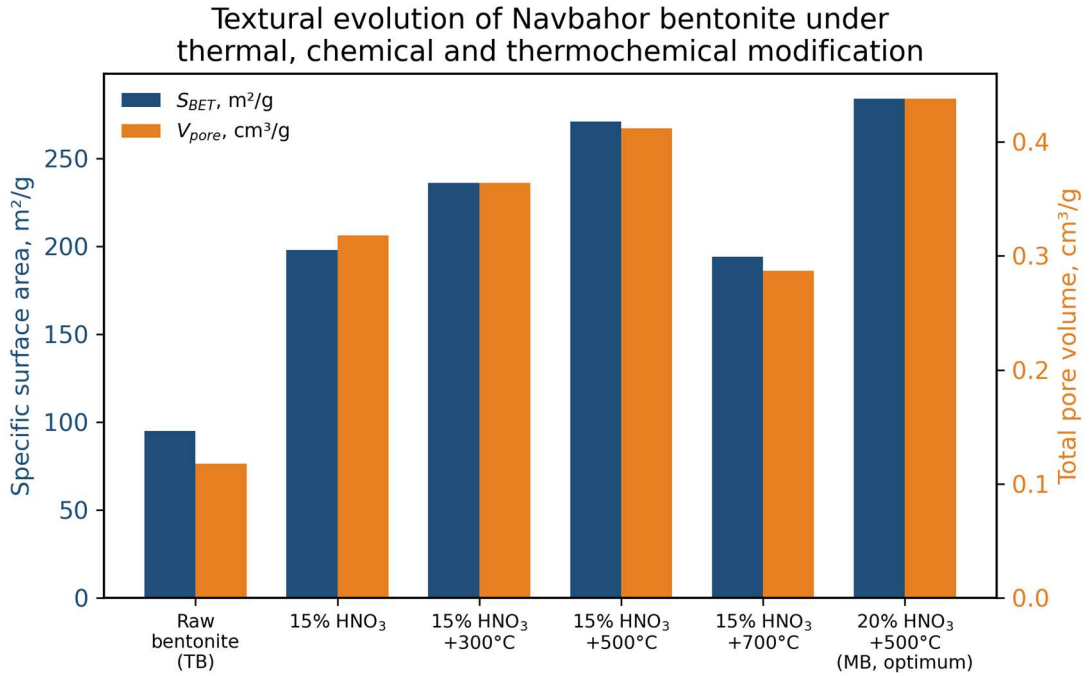


Fig. 3. Textural evolution of Navbahor bentonite under thermal, chemical and combined thermochemical modification.

Table 6.

Textural parameters of Navbahor bentonite modified by different thermochemical protocols

Modification condition	S_{BET}, m²/g	Total pore volume, cm³/g	Mesopore fraction, %	Average pore diameter, nm
Raw bentonite (TB)	95	0.118	67	6.8
15% HNO_3	198	0.318	83	10.0
15% HNO_3 + 300°C	236	0.364	86	11.2
15% HNO_3 + 500°C	271	0.412	89	12.4
15% HNO_3 + 700°C	194	0.287	73	14.8
20% HNO_3 + 500°C (MB, optimum)	284	0.438	91	13.1

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The pore-size distribution obtained from the same N_2 adsorption-desorption data (BJH method) clarifies the mechanism behind this optimum (Table 6a). As the calcination temperature rises from ambient to 500°C, the micropore fraction (<2 nm) increases steadily from 18% to 31% and the mesopore fraction (2-50 nm) remains dominant (64-70%), while the macropore fraction (>50 nm) falls to a minimum of about 5%, reflecting progressive opening of fine porosity without loss of the mesoporous framework. Above 600°C, this trend reverses sharply: the micropore fraction collapses to 16% at 800°C while the macropore fraction rises to 33%, consistent with pore coalescence and the onset of sintering identified in Table 4, and confirming that 400-500°C is the thermodynamically and texturally optimal calcination window for this clay.

Table 6a.

Temperature dependence of the micro-, meso- and macropore fractions of Navbahor bentonite (BJH analysis)

Temperature, °C	Micropores <2 nm, %	Mesopores 2-50 nm, %	Macropores >50 nm, %
Raw bentonite	18	67	15
100	20	68	12
200	23	70	7
300	26	69	5
400	29	66	5
500	31	64	5
600	27	61	12
700	22	57	21
800	16	51	33

3.5. Structural characterization of the modified bentonite (FTIR, DTA/TG, EDXRF)

FTIR spectra of the natural bentonite showed characteristic bands at 507-455 cm^{-1} (Si-O-Al / Al-O-Si framework vibrations), 536 and 526 cm^{-1} (Si-O-Al and Al-O-Si bonds typical of montmorillonite), 476 and 445 cm^{-1} (Fe-O and Al-O bonds) and 795-780 cm^{-1} (quartz impurity), confirming a montmorillonite-dominated aluminosilicate structure. After thermochemical modification, the Si-O-Si silicate framework was preserved (1000-1050 cm^{-1}), while the intensity of the Al-Al-OH deformation band at 914 cm^{-1} decreased, indicating partial

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dealumination and dehydroxylation; the persistence of the 794.7 cm^{-1} quartz band confirmed the stability of the silica phase throughout the treatment.

Derivatographic (TG/DTG/DTA) analysis of the natural bentonite showed a small mass loss at 50-150°C (loss of physisorbed water), minor effects at 200-400°C (loss of cation-bound water and decomposition of organic impurities) and a pronounced mass loss at 500-700°C corresponding to dehydroxylation of structural OH groups. In the thermochemically modified sample, the low-temperature mass loss (100-200°C) was larger, consistent with the higher hydrophilicity and porosity generated by acid activation, while the dehydroxylation step (500-650°C) was more intense, reflecting the larger number of reactive functional groups introduced by the combined treatment.

EDXRF analysis (Table 7) confirmed a progressive increase in the relative SiO_2 content, from 57.9% in the raw clay to 70.4% after treatment with 20% HNO_3, accompanied by a decrease in Al_2O_3 (16.4 → 12.5%), Fe_2O_3 (5.8 → 3.7%), MgO (3.1 → 1.1%), CaO (2.8 → 0.4%) and Na_2O (2.6 → 0.3%). Magnesium fell below the detection limit after modification, confirming near-complete removal of Mg^{2+} from the octahedral sheet – a hallmark of effective acid activation. These compositional changes are fully consistent with the FTIR and textural results and confirm that the thermochemically modified Navbahor bentonite is a high-silica, mesoporous aluminosilicate adsorbent with a substantially enlarged number of surface-active sites.

Table 7.

Change in the chemical composition of Navbahor bentonite during chemical (HNO_3) modification, wt.%

Component, %	Raw bentonite	5% HNO_3	15% HNO_3	20% HNO_3
SiO_2	57.9	60.4	66.8	70.4
Al_2O_3	16.4	15.1	13.2	12.5
Fe_2O_3	5.8	5.1	4.2	3.7
MgO	3.1	2.4	1.6	1.1
CaO	2.8	1.9	0.9	0.4
Na_2O	2.6	1.7	0.8	0.3
K_2O	1.5	1.3	1.0	0.8

3.6. Adsorption isotherms and mechanism for oil products, Fe^{3+}, Cl^- and NH^{4+}

Batch equilibrium data for all four contaminants were well described by the Langmuir model (R^2 = 0.980-0.995), indicating predominantly monolayer

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adsorption on energetically near-uniform sites, while the Freundlich model also gave a satisfactory fit (R^2 = 0.958-0.988) with 1/n < 1 in every case, confirming favourable adsorption on a moderately heterogeneous surface (Table 8, Fig. 4). Thermochemical modification increased the maximum Langmuir capacity (qm) by factors of 3.9 (oil products, 35.2 → 136.8 mg/g), 2.8 (Fe3+, 38.5 → 107.2 mg/g), 3.9 (Cl^-, 15.4 → 59.5 mg/g) and 3.2 (NH^{4+}, 47.6 → 150.3 mg/g); the corresponding Freundlich KF values increased 3.9-5.9-fold, providing independent confirmation of the enhanced adsorption capacity.

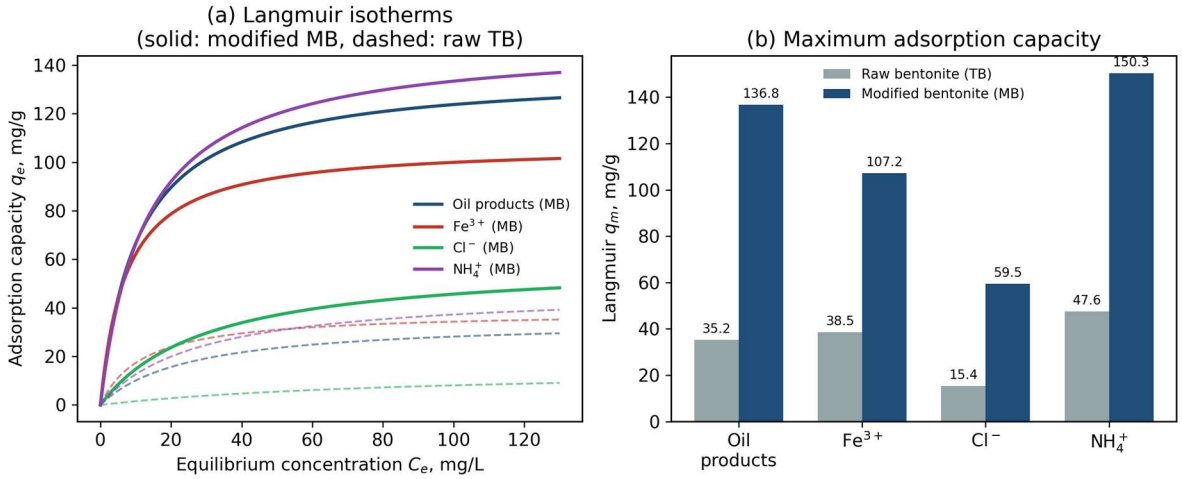


Fig. 4. (a) Langmuir isotherms of oil products, Fe^{3+}, Cl^- and NH^{4+} on raw (TB, dashed) and thermochemically modified (MB, solid) Navbahor bentonite; (b) comparison of the Langmuir maximum adsorption capacities.

Table 8.

Langmuir and Freundlich isotherm parameters for oil products, Fe^{3+}, Cl^- and NH^{4+} on raw (TB) and modified (MB) Navbahor bentonite

Adsorbate	Sample	q_m, mg/g	KL, L/mg	R^2 (Langmuir)	KF, mg/g	R^2 (Freundlich)
Oil products	TB	35.2	0.040	0.985	4.85	0.962
Oil products	MB	136.8	0.095	0.994	27.50	0.981
Fe^{3+}	TB	38.5	0.082	0.989	7.65	0.974
Fe^{3+}	MB	107.2	0.138	0.995	29.80	0.986
Cl^-	TB	15.4	0.011	0.980	1.38	0.958
Cl^-	MB	59.5	0.033	0.992	8.15	0.981
NH^{4+}	TB	47.6	0.036	0.987	8.12	0.969

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Adsorbate	Sample	q_m, mg/g	KL, L/mg	R^2 (Langmuir)	KF, mg/g	R^2 (Freundlich)
NH^{4+}	MB	150.3	0.079	0.995	33.40	0.988

The mechanistic origin of these improvements differs somewhat between adsorbates. Oil-product uptake is governed largely by hydrophobic interactions with the Si-OH groups generated during acid activation and by physical entrapment within the newly developed micro- and mesopores, which provide additional access channels for hydrocarbon molecules [26,27]. Fe^{3+} removal proceeds mainly by cation exchange and coordination at the unsaturated sites left by Al^{3+} removal from the octahedral sheet, which is consistent with the measured qm for raw bentonite (38.5 mg/g) closely matching a literature value of 37.7 mg/g for a comparable untreated clay [28]. Cl^- adsorption on the naturally cation-selective bentonite surface is intrinsically limited, but protonation of newly formed Al-OH and Si-OH groups on MB to $Al\text{-}OH^{2+}$ and $Si\text{-}OH^{2+}$ generates positively charged sites capable of electrostatically binding Cl^- [29,30]. Finally, NH^{4+}, with an ionic radius (1.48 Å) close to that of Na^+ (1.02 Å) and a matching valence, is readily exchanged into the expanded montmorillonite interlayer space, and its 3.2-fold capacity increase closely tracks the 34% increase in cation-exchange capacity (88 → 118 mEq/100 g) measured for MB [31].

3.7. Combined coagulation-flocculation-adsorption treatment of real refinery wastewater

The raw wastewater sampled from the Bukhara Oil Refinery (Table 9, influent column) exceeded regulatory limits for nearly every parameter measured (oil products, suspended solids, total iron, chloride, TDS and ammonium), confirming the need for a multi-stage treatment scheme. In the coagulation stage, increasing the $Al_2(SO_4)_3$ dose from 20 to 100 mg/L raised the removal of suspended solids from 48.5% to 92.3% (Fig. 5); above 100 mg/L, efficiency decreased slightly owing to charge reversal (restabilization) of the colloidal particles, so 100 mg/L was selected as the optimum coagulant dose.

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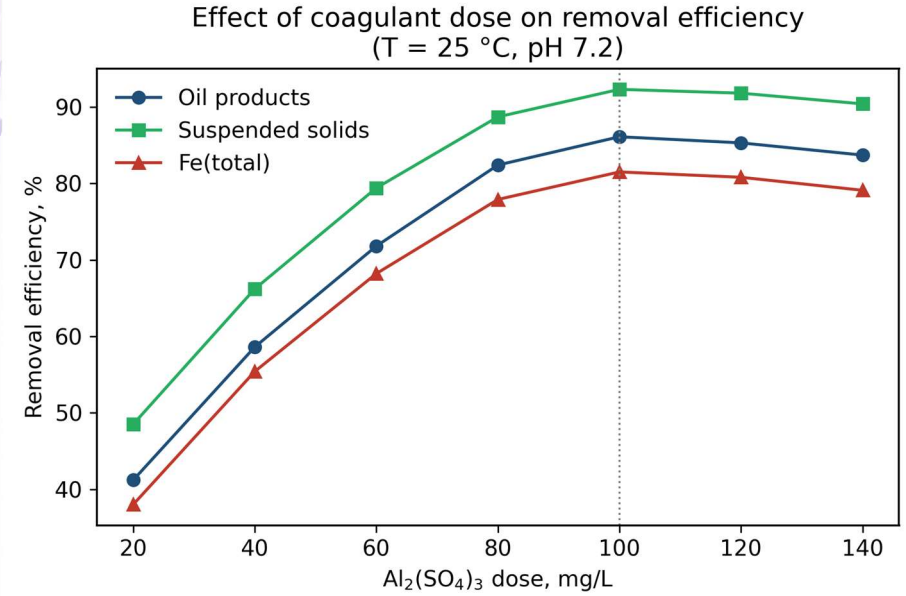


Fig. 5. Effect of coagulant ($Al_2(SO_4)_3$) dose on the removal efficiency of oil products, suspended solids and total iron (T = 25°C, pH 7.2).

In the flocculation stage, the optimum Na-CMC dose was found to be 2.5 mg/L, beyond which floc size and settling rate no longer improved; the settling rate of the flocs increased with temperature over 293-323 K and was strongly pH-dependent, reaching a maximum increase of 67-73% under alkaline conditions. In the adsorption stage, an MB dose of 5 g/L and a contact time of 120 min were found sufficient to bring the residual concentrations of dissolved contaminants close to their equilibrium (isotherm-predicted) values, and the optimum pH range for the overall process was 6.0-7.0.

Under these optimized conditions (100 mg/L coagulant, 2.5 mg/L flocculant, 5 g/L MB adsorbent, pH 6.0-7.0, 120 min contact), the combined three-stage treatment reduced all measured parameters below the regulatory discharge limits (Table 9, Fig. 6): oil products from 86.4 to 1.9 mg/L (97.8% removal), total iron from 12.8 to 0.59 mg/L (95.4%), suspended solids from 420 to 12 mg/L (97.1%), ammonium from 48.5 to 4.3 mg/L (91.2%), COD from 1180 to 138 mg/L (88.3%), chloride from 640 to 137 mg/L (78.6%) and TDS from 3850 to 980 mg/L (74.5%).

Table 9.

Composition of raw and treated wastewater after the combined coagulation-flocculation-adsorption process

Parameter	Influent, mg/L	Effluent, mg/L	Discharge limit, mg/L	Removal, %
Oil products	86.4	1.9	≤ 5.0	97.8
Total iron	12.8	0.59	≤ 0.3-1.0	95.4

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Parameter	Influent, mg/L	Effluent, mg/L	Discharge limit, mg/L	Removal, %
Chloride (Cl^-)	640	137	≤ 250	78.6
Ammonium (NH^{4+})	48.5	4.3	≤ 5.0	91.2
Suspended solids	420	12	≤ 15	97.1
Total dissolved solids	3850	980	≤ 1000	74.5
COD	1180	138	≤ 150	88.3
pH	7.8	7.2	6.5-8.5	–

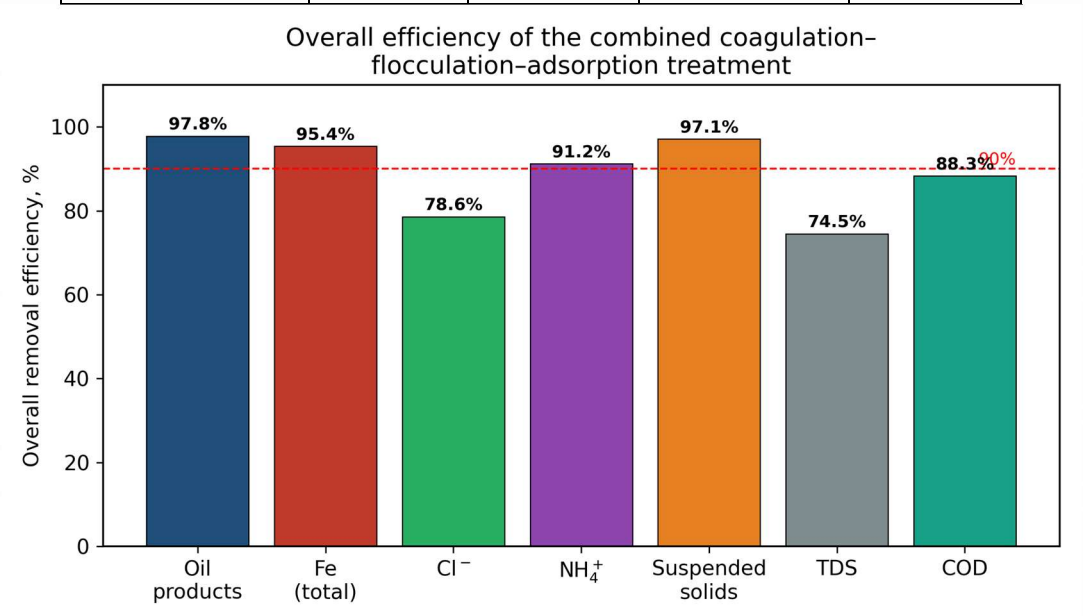


Fig. 6. Overall removal efficiency of the combined coagulation-flocculation-adsorption treatment for each monitored parameter.

The comparatively lower removal of chloride (78.6%) and TDS (74.5%) reflects the intrinsically limited capacity of an aluminosilicate adsorbent for highly soluble, non-specifically adsorbed ions, which are removed mainly through electrostatic interaction with protonated surface groups rather than through the stronger cation-exchange and coordination mechanisms available to Fe^{3+} and NH^{4+}; nonetheless, both parameters were brought within their respective regulatory limits. The synergy between the three stages is noteworthy: coagulation and flocculation remove the bulk of the colloidal load and free/emulsified oil before the water reaches the adsorption stage, which prevents premature pore blockage of the

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bentonite and preserves its adsorption capacity for the dissolved ionic contaminants (Fe^{3+}, Cl^{-}, NH^{4+}), so that the efficiency of the combined process exceeds what would be expected from the individual stages applied separately.

3.8. Comparison with the literature and practical significance

The maximum adsorption capacities obtained for thermochemically modified Navbahor bentonite (136.8 mg/g for oil products, 107.2 mg/g for Fe^{3+}) are comparable with, or exceed, values reported for magnetically modified and carbon-combined bentonite adsorbents used for diesel-oil and heavy-metal removal in other studies [26-30], while requiring only a simple, two-stage acid-thermal protocol and no imported reagents other than technical-grade nitric acid, which is manufactured domestically. Given that the specific surface area of raw Navbahor bentonite already approaches that of imported reference clays (Table 2), and that thermochemical modification nearly triples this value while more than tripling the pore volume, the developed technology offers a resource-efficient route to replacing imported sorbents in the petroleum-refining industry with a Uzbekistan-sourced alternative, consistent with recent industrial-development priorities in the country [36,37].

3.9. Pilot-scale validation at the Bukhara Oil Refinery

To verify that the laboratory-scale results translate into a real industrial setting, the modified bentonite (MB) was tested directly at the physico-chemical treatment unit of the Bukhara Oil Refinery, in cooperation with the plant's ecology laboratory. Mechanically pre-treated wastewater was split into parallel streams: (i) a control (no reagent), (ii) the technology currently used at the plant (aluminium sulphate coagulant with polyacrylamide flocculant) and (iii) the newly developed technology (MB adsorbent with Na-CMC flocculant and a small dose of $Ca(OH)_2$ to promote settling). In a first trial, an excessive $Ca(OH)_2$ dose raised the pH of the treated water to 9.5-10, which is unfavourable for the downstream biological treatment stage; the lime dose was therefore reduced from 40 to 10 mL of a 10% solution in a second trial, stabilizing the pH at about 7.5 without loss of treatment performance.

Under the optimized second-trial conditions, the MB-based technology consistently outperformed the plant's existing aluminium-sulphate technology on identical raw wastewater (Table 10): the residual oil-product concentration was reduced to 6.4 mg/L versus 8.4 mg/L for the existing technology (a 23.8% relative improvement), suspended solids to 33.3 mg/L versus 58.0 mg/L (42.6% improvement), and total iron to 2.0 mg/L versus 2.5 mg/L (20% improvement); chloride and total dissolved solids were also reduced further, although by smaller margins (12.8% and 0.2%, respectively), consistent with the comparatively limited affinity of an aluminosilicate adsorbent for these highly soluble species discussed

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in Section 3.6. Flocs formed with the MB-based reagent system settled faster and produced a denser, more compact sludge than those formed with the conventional coagulant, and the clarified water showed noticeably improved transparency.

Table 10.

Comparison of the existing ($Al_2(SO_4)_3$-based) and newly developed (MB-based) treatment technologies on real Bukhara Oil Refinery wastewater (second-stage pilot trial)

Parameter	Raw wastewater	Existing technology	MB-based technology	Additional improvement
Oil products, mg/L	22.8	8.4	6.4	23.8%
Suspended solids, mg/L	61.7	58.0	33.3	42.6%
Total iron, mg/L	3.2	2.5	2.0	20.0%
Chloride, mg/L	607	601	524	12.8%
Total dissolved solids, mg/L	1828	1788	1784	0.2%

These pilot-scale results confirm that the advantages of thermochemically modified Navbahor bentonite observed in controlled batch experiments (Sections 3.6-3.7) are reproducible under real operating conditions with actual, highly variable refinery wastewater, and that the reagent dosing (including the auxiliary lime dose used to promote settling) can be tuned to avoid an excessively alkaline effluent that would otherwise compromise subsequent biological treatment. Before full industrial implementation, continuous pilot-plant trials and complete monitoring of biochemical oxygen demand (BOD), COD, heavy metals and other regulated parameters are recommended.

4. INDUSTRIAL-SCALE PRODUCTION TECHNOLOGY AND ECONOMIC EVALUATION

4.1. Process design and optimized production parameters

On the basis of the single-factor optimization described in Sections 3.2-3.4, a two-stage production technology for thermochemically modified bentonite was designed for direct integration into the wastewater-treatment system of the Bukhara Oil Refinery. In the first (chemical) stage, natural Navbahor bentonite reacts with

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a 20% HNO_3 solution (solid:liquid = 1:3.5) at 80-90°C for 4 h, during which part of the structural Al, Fe and Mg oxides pass into solution, exchangeable cations are released, and new silanol (≡Si-OH) and aluminol (≡Al-OH) surface groups are formed – the same functional groups identified by FTIR (Section 3.5) as primary adsorption sites for heavy-metal ions, ammonium and oil-product molecules. The acid-treated slurry is filtered and washed with process water in several steps until the filtrate reaches pH 6.0-6.5, ensuring complete removal of residual HNO_3 and dissolved metal nitrates and providing a stable feed for the subsequent thermal stage. In the second (thermal) stage, the washed cake is pre-dried at 15°C to reduce moisture from 40-42% to 8-10%, and then calcined in a rotary kiln at 500°C for 45-60 min, which removes adsorbed and structural water, widens the interlayer spacing and substantially develops the mesopore network, consistent with the textural evolution reported in Table 6. The finished product is cooled, milled and classified to a working particle size of 0.1-2 mm before packaging.

Table 11.

Optimized parameters of the industrial-scale thermochemical modification process

Parameter	Selected value
HNO_3 concentration	20%
Chemical activation temperature	80-90°C
Chemical activation time	4 h
Solid:liquid ratio	1:3.5
Final wash-water pH	6.0-6.5
Pre-drying temperature	150°C
Calcination (thermal activation) temperature	500°C
Calcination time	45-60 min
Finished-product moisture content	≤ 2%

The plant-integrated process flow comprises eleven principal unit operations: a receiving and storage hopper for raw bentonite (B-1); an acid-preparation reactor for the 20% HNO_3 working solution (R-1); a process-water storage tank (H-1); the acid-activation reactor (R-2), in which Al_2O_3, Fe_2O_3 and MgO are partially dissolved; a first filter press (F-1) separating the acid filtrate (recycled or neutralized) from the wet cake; a washing tank (J-1) that removes residual acid and dissolved metal nitrates; a second filter press (F-2); a rotary drum

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dryer (Q-1) reducing moisture from about 40% to 8-10%; a rotary calcination kiln (P-1, together with a hot-air generator) operating at 400-500°C, where thermal activation develops the adsorption centres and mesoporous structure; a cooler (S-1) that lowers the product temperature from 400-500°C to 40-50°C prior to size reduction; a final crusher (D-2) and classifier (K-1) that produce a uniform 0.1-2 mm working fraction (oversize particles being recycled to the crusher); and a dosing/packaging unit (U-1, 25 kg polypropylene bags or big-bags) feeding the finished-product warehouse (O-1). This modular scheme allows the technology to be readily scaled beyond the pilot capacity described below, using the same unit operations at larger throughput.

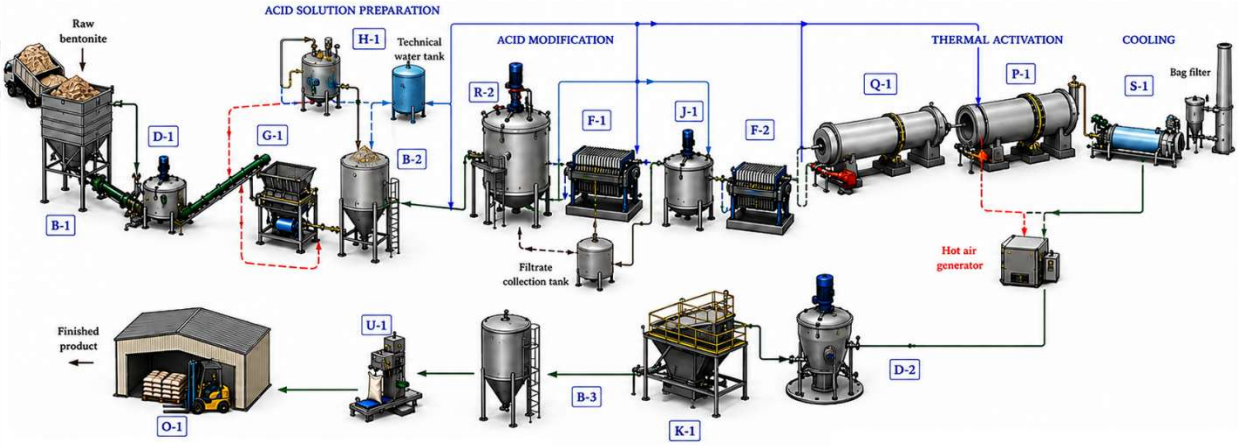


Fig. 7. Process flow diagram of the proposed industrial-scale production line for thermochemically modified Navbahor bentonite. Equipment codes: *B-1 – raw-bentonite receiving/storage hopper; D-1 – primary crusher; G-1 – vibrating screen; E-1 – belt conveyor; B-2 – intermediate (buffer) hopper; R-1 – 20% HNO_3 solution-preparation reactor; H-1 – process-water tank; R-2 – acid-activation reactor; F-1, F-2 – first/second-stage filter presses; T-1 – filtrate collection tank; J-1 – washing tank; N-1 – neutralization tank; Q-1 – rotary drum dryer; HG-1 – hot-air generator; P-1 – rotary calcination kiln; S-1 – cooler; CY-1 – cyclone; MF-1 – fabric filter; EX-1 – aspiration fan; CH-1 – stack; D-2 – final crusher; K-1 – vibrating classifier (0.1-2 mm); K-3 – elevator/conveyor; B-3 – finished-product hopper; U-1 – dosing/packaging unit; O-1 – finished-product warehouse.*

4.2. Production capacity and material balance

The required adsorbent dose was set at 5 g/m^3 (5 mg/L) of treated wastewater, in line with the optimum adsorption-stage parameters established in Section 3.7. Given an average wastewater flow of 1300 m^3/day at the Bukhara Oil Refinery, the daily and annual adsorbent demand were calculated as Qads = 1300 × 1000 × 5 = 6,500,000 mg/day = 6.5 kg/day, i.e. 6.5 × 365 = 2372.5 kg/year ≈ 2.37 t/year. This modest but continuous demand defines the design capacity of the

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proposed production line and confirms that a compact, low-capital installation is sufficient to fully cover the plant's own adsorbent requirement from local raw material.

The corresponding annual material balance (Table 12) shows that production of 2.37 t/year of finished modified bentonite requires 6.07 t of raw bentonite (12% moisture), 5.58 t of concentrated (65%) HNO_3, 12.55 t of dilution water and 18.13 t of wash water as principal inputs, with acid filtrate (14.50 t, containing HNO_3 and dissolved metal salts), wash filtrate (18.60 t), evaporated moisture (1.45 t), thermal off-gases (H_2O, CO_2, NO_x; 0.27 t) and dust/mechanical losses (5.14 t) as the principal outputs, closing at 42.33 t of total annual throughput on both sides of the balance.

Table 12.

Annual material balance of the thermochemically modified bentonite production line (design capacity 2.37 t/year)

Stream	Input, t/year	Output, t/year
Raw bentonite (12% moisture)	6.07	–
Concentrated HNO_3 (65%)	5.58	–
Dilution water	12.55	–
Wash water	18.13	–
Finished modified bentonite	–	2.37
Acid filtrate (HNO_3 + metal salts)	–	14.50
Wash filtrate	–	18.60
Evaporated moisture (drying)	–	1.45
Thermal off-gases (H_2O, CO_2, NO_x)	–	0.27
Dust and mechanical losses	–	5.14
Total	42.33	42.33

4.3. Economic evaluation

A preliminary technical-economic assessment was carried out for the designed production line (Table 13). At the design capacity of 2.37 t/year, operating 365 days/year with a workforce of four, and consuming 111,000 kWh/year of electricity, 16,000 m^3/year of natural gas and 30 m3/year of process water, the total investment (equipment, buildings/infrastructure and installation) was estimated at 3570.5 million UZS, and the annual production cost – comprising raw materials, utilities, wages, social contributions, depreciation (6%), maintenance and

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packaging – at 897.32 million UZS, giving a unit production cost of about 378.62 million UZS per tonne. At an assumed 20% profit margin, the corresponding selling price is 454.34 million UZS/t, yielding an annual revenue of 1076.79 million UZS for the full 2.37 t/year output.

Table 13.

Technical-economic indicators of the proposed thermochemically modified bentonite production line

Indicator	Value
Production capacity	2.37 t/year
Total investment	3570.5 million UZS
Annual production cost	897.32 million UZS
Unit production cost	378.62 million UZS/t
Selling price (20% margin)	454.34 million UZS/t
Annual revenue	1076.79 million UZS
Cost of equivalent imported adsorbent (~850 million UZS/t)	2014.50 million UZS
Net annual economic benefit vs. import substitution	937.71 million UZS
Profitability	20%
Payback period	≈ 3.8 years

The economic benefit of the proposed technology becomes particularly clear when compared with the cost of importing an equivalent quantity of organo-modified bentonite adsorbent, conservatively priced at about 850 million UZS/t on the current market, which would cost the enterprise approximately 2014.50 million UZS/year for the same 2.37 t. Substituting this import with locally produced, thermochemically modified Navbahor bentonite is therefore estimated to generate a net annual economic effect of about 937.71 million UZS, with the initial investment recovered within approximately 3.8 years at the stated 20% profitability. Beyond the direct cost saving, import substitution also reduces the enterprise's exposure to currency and supply-chain risk and makes productive use of an abundant domestic mineral resource, in line with the national strategy of expanding domestic innovation-driven industrial capacity referenced in Section 1.

5. CONCLUSIONS.

Systematic thermal, chemical and thermochemical activation of natural Navbahor bentonite established that: (i) calcination alone develops an optimum

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textural structure at 500°C (SBET = 193 m^2/g, pore volume 0.264 cm^3/g); (ii) acid activation alone reaches an optimum at 20% HNO3 (SBET = 214 m^2/g, pore volume 0.347 cm^3/g); and (iii) combining 20% HNO3 activation with subsequent calcination at 500°C produces a substantially more effective adsorbent (MB), with SBET = 284 m^2/g (2.99-fold increase), total pore volume = 0.438 cm^3/g (3.71-fold increase), mesopore fraction of 91% and cation-exchange capacity increased from 88 to 118 mEq/100 g, confirmed by FTIR, DTA/TG and EDXRF analysis showing progressive dealumination, dehydroxylation and enrichment of the silica framework.

Batch adsorption experiments fitted the Langmuir model well (R^2 = 0.980-0.995) and showed that thermochemical modification increased the maximum adsorption capacity by 2.8-3.9-fold for oil products (136.8 mg/g), Fe^{3+} (107.2 mg/g), Cl^- (59.5 mg/g) and NH^{4+} (150.3 mg/g) relative to the untreated clay, with the improvements explained by a combination of hydrophobic interaction, cation exchange, coordination at dealuminated sites and electrostatic interaction with protonated surface groups, depending on the adsorbate.

A three-stage combined coagulation ($Al_2(SO_4)_3$, 100 mg/L) - flocculation (Na-CMC, 2.5 mg/L) - adsorption (modified bentonite, 5 g/L, 120 min, pH 6.0-7.0) process applied to real Bukhara Oil Refinery wastewater achieved removal efficiencies of 97.8% (oil products), 97.1% (suspended solids), 95.4% (iron), 91.2% (ammonium), 88.3% (COD), 78.6% (chloride) and 74.5% (total dissolved solids), bringing every monitored parameter below the applicable regulatory discharge limits. Independent pilot-scale trials conducted directly at the refinery's treatment unit confirmed that the modified-bentonite technology outperformed the plant's existing aluminium-sulphate-based process by 23.8% (oil products), 42.6% (suspended solids) and 20% (iron), while allowing the process pH to be stabilized at about 7.5, a favourable condition for the downstream biological treatment stage.

A complete production technology was designed around these optimized parameters, comprising acid activation, filtration/washing, drying, rotary-kiln calcination, cooling, milling, classification and packaging. For the Bukhara Oil Refinery (wastewater flow 1300 m^3/day, adsorbent dose 5 g/m^3), the required production capacity is 2.37 t/year, achievable with a total investment of about 3570.5 million UZS and an annual production cost of about 897.32 million UZS. Replacing an equivalent quantity of imported organo-modified bentonite (estimated cost 2014.50 million UZS/year) with the locally produced adsorbent yields an estimated net annual economic benefit of 937.71 million UZS at 20% profitability, with a payback period of approximately 3.8 years.

Taken together, these results demonstrate that thermochemically activated local Navbahor bentonite is a technically effective, low-cost, and environmentally

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and economically sound substitute for imported adsorbents in the treatment of complex petroleum-refinery wastewater, and provide both the scientific and the engineering-economic basis needed to scale up the developed technology to full industrial application.

Author contributions

Conceptualization and methodology: N.K. Sadikova, R.R. Khayitov; investigation and formal analysis: N.K. Sadikova; supervision: R.R. Khayitov; writing – original draft: N.K. Sadikova; writing – review and editing: N.K. Sadikova, R.R. Khayitov. All authors have read and agreed to the published version of the manuscript.

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Data availability

The data presented in this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest.

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