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CORN-COB-DERIVED FE-MODIFIED ACTIVATED CARBONS FOR PARACETAMOL AND SULFAMETHOXAZOLE REMOVAL BY ADSORPTION AND OXIDATIVE TREATMENT

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Abstract. Fe-modified activated carbons were prepared from corn-cob-derived activated carbon by wet impregnation with ferric nitrate, followed by thermal treatment under nitrogen. The obtained materials, denoted MAC1, MAC2.5, and MAC5 according to their nominal iron loadings, were evaluated for the aqueous-phase removal of paracetamol (PCM) and sulfamethoxazole (SMX) by adsorption and oxidant-assisted treatment using hydrogen peroxide and sodium persulfate (SPS). The experiments were conducted with an initial pollutant concentration of 50 mg L⁻¹, a material dose of 2.5 g L⁻¹, pH 3.5, and 60 °C for up to 24 h. Hydrogen peroxide and SPS were each used at an initial mass concentration of 44.3 mg L⁻¹, corresponding to 1.30 mmol L⁻¹ H₂O₂ and 0.186 mmol L⁻¹ Na₂S₂O₈. The residual oxidant concentration

was monitored during treatment, and samples were chemically quenched before HPLC analysis. Under the tested model-water conditions, the highest experimental adsorption uptake was 17.08 mg g⁻¹ for PCM on MAC5 and 7.52 mg g⁻¹ for SMX on MAC2.5. The SPS-assisted systems produced a greater decrease in the aqueous concentration of the parent compounds than the hydrogen-peroxide-assisted systems, with PCM removal above 98% and SMX removal up to 74% after 24 h. These values represent aqueous-phase removal and do not by themselves distinguish adsorption from chemical transformation. The results indicate that iron loading, porous structure, pollutant speciation, and oxidant consumption jointly influence the observed performance.

Keywords: corn cob; Fe-modified activated carbon; paracetamol; sulfamethoxazole; hydrogen peroxide; sodium persulfate; adsorption; oxidative treatment

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ЖҮГЕРІ СОБЫҚТАРЫНАН АЛЫНҒАН ТЕМІРМЕН МОДИФИКАЦИЯЛАНҒАН БЕЛСЕНДІРІЛГЕН КӨМІРЛЕРМЕН ПАРАЦЕТАМОЛ МЕН СУЛЬФАМЕТОКСАЗОЛДЫ АДСОРБЦИЯЛЫҚ- ТОТЫҒУ ЖОЛЫМЕН ЖОЮ

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Аннотация. Темірмен модификацияланған белсендірілген көмірлер жүгері собықтарынан алынған белсендірілген көмірді темір (III) нитратымен ылғалды импрегнациялау және кейіннен азот атмосферасында термиялық өңдеу арқылы дайындалды. Темірдің номиналды мөлшеріне сәйкес MAC1, MAC2.5 және MAC5 деп белгіленген алынған материалдар парацетамолды (PCM) және сульфаметоксазолды (SMX) су фазасынан адсорбция және сутек пероксиді мен натрий персульфатын (SPS) қолдану арқылы тотықтырғыш өңдеу әдістерімен жою үшін зерттелді. Тәжірибелер ластаушы заттың бастапқы концентрациясы $50 \text{ мг} \cdot \text{л}^{-1}$, материал мөлшері $2,5 \text{ г} \cdot \text{л}^{-1}$, pH 3,5 және 60°C температура жағдайында 24 сағатқа дейін жүргізілді. Сутек пероксиді мен SPS-тің бастапқы массалық концентрациясы бірдей, яғни $44,3 \text{ мг} \cdot \text{л}^{-1}$ болды, бұл сәйкесінше $1,30 \text{ ммоль} \cdot \text{л}^{-1} \text{H}_2\text{O}_2$ және $0,186 \text{ ммоль} \cdot \text{л}^{-1} \text{Na}_2\text{S}_2\text{O}_8$ мөлшеріне сәйкес келді. Өңдеу барысында тотықтырғыштың қалдық концентрациясы бақыланды, ал ЖТСХ талдауының алдында үлгілердегі реакция химиялық жолмен тоқтатылды. Зерттелген модельдік су жүйесі жағдайында ең жоғары тәжірибелік адсорбциялық сыйымдылық PCM үшін MAC5 материалында $17,08 \text{ мг} \cdot \text{г}^{-1}$, ал SMX үшін MAC2.5 материалында $7,52 \text{ мг} \cdot \text{г}^{-1}$ құрады. SPS қатысқан жүйелер сутек пероксиді қолданылған жүйелермен салыстырғанда бастапқы қосылыстардың су фазасындағы концентрациясының анағұрлым айқын төмендеуін қамтамасыз етті: 24 сағаттан кейін PCM жойылу дәрежесі 98%-дан жоғары, ал SMX үшін 74%-ға дейін жетті. Бұл мәндер қосылыстардың су фазасынан жалпы жойылуын сипаттайды және өздігінен адсорбция мен химиялық түрленудің үлесін ажыратуға мүмкіндік бермейді. Нәтижелер темір мөлшері, кеуекті құрылым, ластаушы заттардың ерітіндідегі күйі және тотықтырғыштың жұмсалуды байқалған үдеріс тиімділігіне бірлесіп әсер ететінін көрсетеді.

Түйін сөздер: жүгері собықтары; темірмен модификацияланған белсендірілген көмір; парацетамол; сульфаметоксазол; сутек пероксиді; натрий персульфаты; адсорбция; тотықтырғыш өңдеу

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МОДИФИЦИРОВАННЫЕ ЖЕЛЕЗОМ АКТИВИРОВАННЫЕ УГЛИ ИЗ КУКУРУЗНЫХ ПОЧАТКОВ ДЛЯ АДСОРБЦИОННО- ОКИСЛИТЕЛЬНОГО УДАЛЕНИЯ ПАРАЦЕТАМОЛА И СУЛЬФАМЕТОКСАЗОЛА

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Аннотация. Модифицированные железом активированные угли были получены на основе активированного угля из кукурузных початков методом влажной импрегнации нитратом железа(III) с последующей термической обработкой в атмосфере азота. Полученные материалы, обозначенные как MAC1, MAC2.5 и MAC5 в соответствии с номинальным содержанием железа, были исследованы для удаления парацетамола (PCM) и сульфаметоксазола (SMX) из водной фазы посредством адсорбции и окислительной обработки с использованием пероксида водорода и персульфата натрия (SPS). Эксперименты проводили при начальной концентрации загрязняющего вещества 50 мг·л⁻¹, дозировке материала 2,5 г·л⁻¹, pH 3,5 и температуре 60 °C в течение до 24 ч. Пероксид водорода и SPS использовали при одинаковой начальной массовой концентрации 44,3 мг·л⁻¹, что соответствовало 1,30 ммоль·л⁻¹ H₂O₂ и 0,186 ммоль·л⁻¹ Na₂S₂O₈ соответственно. В ходе обработки контролировали остаточную концентрацию окислителя, а перед ВЭЖХ-анализом образцы подвергали химическому гашению реакции. В исследованных условиях модельной водной системы максимальная экспериментальная адсорбционная ёмкость составила 17,08 мг·г⁻¹ для PCM на MAC5 и 7,52 мг·г⁻¹ для SMX на MAC2.5. Системы с

использованием SPS обеспечивали более значительное снижение концентрации исходных соединений в водной фазе по сравнению с системами, содержащими пероксид водорода: степень удаления РСМ превышала 98%, а SMX достигала 74% через 24 ч. Указанные значения характеризуют удаление соединений из водной фазы и сами по себе не позволяют разграничить вклад адсорбции и химической трансформации. Полученные результаты показывают, что содержание железа, пористая структура, форма нахождения загрязняющего вещества в растворе и расход окислителя в совокупности определяют наблюдаемую эффективность процесса.

Ключевые слова: кукурузные початки; активированный уголь, модифицированный железом; парацетамол; сульфаметоксазол; пероксид водорода; персульфат натрия; адсорбция; окислительная обработка.

Introduction. Contaminants of emerging concern (CECs), including pharmaceuticals, personal care products and other bioactive organic compounds, are increasingly detected in surface waters, groundwater and treated effluents, raising concerns due to their persistence and potential ecological and human health impacts (Rocha et al., 2021; Song, et al., 2023; Vaddi et al., 2024). Conventional wastewater treatment processes are often insufficient for complete removal of these micropollutants, which has stimulated growing interest in advanced materials capable of combining high removal efficiency with operational simplicity and reusability.

In the literature, magnetic activated carbons (MACs) have emerged as multifunctional materials that integrate the high adsorption capacity of activated carbons with magnetic separability, enabling both efficient CECs removal and facile post-treatment recovery when magnetic properties are directly demonstrated (Pereira D. et al, 2022). Beyond acting as sorbents, such materials can also serve as catalysts or catalyst supports in advanced oxidation processes (AOPs), positioning them as promising platforms for integrated adsorption–oxidation water treatment strategies (Moosavi et al., 2020; Çako et al., 2024).

Literature review. MACs are commonly synthesized by introducing iron oxides, predominantly magnetite (Fe_3O_4) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$), onto activated carbon, biochar or related carbonaceous matrices via co-precipitation, impregnation, infiltration or in-situ composite formation routes (Pereira D. et al, 2020; Rocha L. et al 2020). A wide range of waste-derived precursors, such as paper mill sludge, agricultural residues, cellulosic wastes and rice husk, have been successfully employed, aligning MACs development with principles of resource recovery and sustainability. Properly designed MACs typically retain high specific surface areas ($\approx 550\text{--}800\text{ m}^2\text{ g}^{-1}$) while achieving saturation magnetizations in the range of $19\text{--}40\text{ emu g}^{-1}$, allowing rapid magnetic separation without severe loss of porosity or adsorption sites (Pereira et al., 2020).

As adsorbents, MACs exhibit fast kinetics and high uptake capacities toward a wide spectrum of CECs, including pharmaceuticals and other aromatic and heterocyclic compounds, in both model solutions and real wastewater matrices. Adsorption

equilibrium is frequently reached within 30–60 min and is commonly described by Langmuir or Freundlich isotherms, while pseudo-second-order kinetic models often provide the best fit, indicating contributions from chemisorption and surface complexation (Baghdadi et al., 2016). Although competition from natural organic matter and variations in pH in real effluents can reduce adsorption capacities, MACs generally retain substantial removal efficiency under realistic conditions. Moreover, MACs derived from commercial powdered activated carbons and regenerated via inductive or microwave heating have demonstrated stable CECs removal over multiple adsorption–desorption cycles with only minor performance losses (Pereira et al., 2022; Pereira et al., 2020).

In addition to adsorption, MACs have been widely explored as heterogeneous catalysts in peroxide-based AOPs. Magnetite-loaded activated carbons act as Fenton-like catalysts, activating hydrogen peroxide to generate reactive oxygen species capable to degrade a wide range of organic pollutants, while partially regenerating the carbon surface during oxidation. Compared with homogeneous iron systems, supported magnetic carbons facilitate catalyst recovery and significantly limit iron leaching, although excessive iron loading may lead to pore blockage and reduced adsorption performance. The efficiency of catalytic wet peroxide oxidation on MACs is strongly influenced by pH (typically mildly acidic), oxidant, catalyst dosages, and reaction temperature (Esteves et al., 2024).

More recently, increasing attention has been directed toward the activation of persulfate-based oxidants by magnetic carbon materials. Carbon-based magnetic nanocomposites, including MACs, magnetic carbon xerogels and ferrite–carbon hybrids, have demonstrated high efficiency in activating sodium persulfate (SPS) and peroxymonosulfate (PMS), enabling both radical and non-radical oxidation pathways for the degradation of persistent CECs (Pang et al., 2019). In these systems, the carbon matrix plays a critical role by dispersing magnetic particles, promoting electron transfer and Fe(III)/Fe(II) cycling, and providing additional catalytic and adsorption sites, particularly in heteroatom-doped carbons. Depending on material composition and operating conditions, pollutant degradation may proceed via sulfate radicals, hydroxyl radicals, superoxide species and/or singlet oxygen pathways (Qin et al., 2024; Tian et al., 2022; Outsiou et al., 2017). Several magnetic carbon-based catalysts, such as Fe/Co-containing carbon xerogels, Prussian blue–carbon composites and self-doped iron–carbon materials derived from waste sources, have shown rapid CECs degradation across broad pH ranges, good reusability and low metal leaching (Qin et al., 2024; Outsiou et al., 2017). Nevertheless, despite extensive laboratory-scale studies, applications in real wastewater matrices remain limited, and mechanistic understanding, particularly regarding non-radical oxidation routes, continues to evolve (Pang et al., 2019).

Fe-modified porous carbons provide a potentially useful platform for combining adsorption with oxidant-assisted treatment. However, the contributions of adsorption, direct oxidant action, heterogeneous surface reactions, and homogeneous reactions involving dissolved iron must be distinguished experimentally. In addition, claims

concerning magnetic separability require direct magnetic measurements, while mechanistic assignments require evidence beyond parent-compound concentration profiles.

The objective of this study was to compare three nominal iron loadings introduced into the same corn-cob-derived activated carbon and to evaluate their performance toward PCM and SMX under adsorption, hydrogen-peroxide-assisted, and SPS-assisted conditions. The work focuses on aqueous-phase removal and on relationships between nominal iron loading, porous characteristics, surface acid-base behavior, and treatment performance. The previously reported MnFe_2O_4 /Shymkent material was used only as a reference comparator.

Materials and Methods. Materials. Paracetamol (PCM, $\geq 99\%$), sulfamethoxazole (SMX, $\geq 99\%$), acetonitrile (HPLC grade, $\geq 99.9\%$), hydrogen peroxide solution ($\geq 30\%$), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 98\%$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium thiosulfate, hydrochloric acid, sodium hydroxide, and sodium chloride were of analytical or chromatographic grade. All reagents were used without further purification.

Characterization of activated carbons and Fe-modified activated carbons.

Textural properties of the obtained materials. The textural properties of the unmodified activated carbon (AC) and the Fe-modified samples were evaluated by N_2 adsorption-desorption at -196°C . AC was analysed using a Micromeritics ASAP 2020 after degassing at 150°C for 12 h, whereas MAC2.5 was analysed using an EASY-V1440 after degassing at 120°C for 2 h and 250°C for 6 h. N_2 -physisorption data were also obtained for MAC1 and MAC5 and are reported in Table 1. The BET specific surface area (SBET), total pore volume (VTotal), micropore volume (Vmicro), mesopore volume (Vmeso), Vmicro/VTotal ratio, and average pore diameter (dpore) were used for comparison.

Surface characteristics and elemental composition of the obtained materials. Elemental CHNS/O analysis was performed on an Elementar Unicube, Germany. The average mass of the analyzed substance was 1-5 mg. The temperature of the combustion column was 1150°C , and the temperature of the recovery column was 850°C . The analysis process in the Elementar Unicube device is based on the classical technique of Pregl–Dumas organic elemental analysis and consists of a series of sequential steps: combustion (reduction), homogenization of products, separation of products and their detection. The sample is burned in the analyzer at a high temperature in the presence of oxygen. During the combustion process, gases (CO_2 , H_2O , N_2 , SO_2) containing the studied elements are released. These gases then pass through various detectors to measure their volume and elemental composition.

Thermogravimetric analysis of the carbon sample was performed using a LabSys Evo thermobalance (Setaram Instrumentation) under nitrogen (50 mL min^{-1}) from 30 to 900°C .

The point of zero charge (pHpzc) was estimated by the pH-drift method. A series of 50 mL portions of 0.01 M NaCl solution was adjusted to initial pH values from 2 to 12 using 0.01 M HCl or 0.01 M NaOH. Then, 0.15 g of material was added to each

flask and equilibrated for 48 h. The final pH was measured, $\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$ was calculated, and pH_{pzc} was taken as the initial pH at which $\Delta\text{pH} = 0$. The resulting pH-drift profiles were used to estimate the surface-charge transition region discussed in the Results section.

Morphological properties of the obtained materials. Morphological structures were analyzed using a scanning electron microscope (Auriga Crossbeam 540, Carl Zeiss, Germany). Prior to analysis, the samples were sputter-coated with a thin layer of carbon using a Carbon Coater AGB7230 (Agar Scientific, UK) to improve surface conductivity. Imaging was performed at accelerating voltages of 10–20 kV at various magnifications. Elemental composition was determined by energy-dispersive X-ray spectroscopy (EDS) using an AStec system.

Methods to obtain activated carbons. The corn-cob-derived activated carbon used as the starting material was prepared (see Fig.1) according to the procedure reported previously (Kurtebayeva et al., 2026).

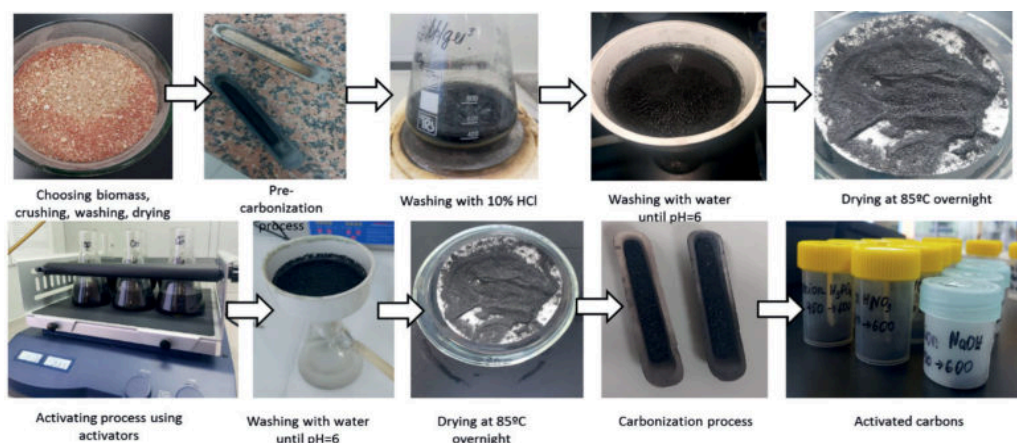


Figure 1 - Scheme of the activated carbons synthesis procedure.

Figure 1. Was used to calculate the yield of the product (activated carbon, AC) after the carbonization process.

$$Y = \frac{m_{\text{AC}}}{m_{\text{raw}}} \cdot 100\% \quad (1)$$

where Y is the dry-basis product yield (%), m_{AC} is the dry mass of activated carbon, and m_{raw} is the dry mass of the initial biomass.

Methods to obtain Fe-modified activated carbons. In this work, modified activated carbons were prepared by wet impregnation of powdered activated carbon (5.0 g aliquots) with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to obtain nominal iron loadings of 1, 2.5 and 5 wt.% (relative to the dry carbon mass). Prior to impregnation, AC was dried at 110 °C for 2 h and cooled in a desiccator. The required mass of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for each loading was calculated stoichiometrically (Equation 2, where m is mass of the salt (g), m_{AC} is mass of activated carbon, ω_{Fe} is the required iron loading, $\omega_{\text{Fe in salt}}$ is the required

mass of iron in the salt) and dissolved in 50 mL of a 50:50 (v/v) water/absolute ethanol solvent to prepare the impregnation solution. The dissolved solution was added to the 5.0 g carbon sample in a beaker and mixed to form a homogeneous slurry. The slurry was gently heated at $\sim 50^\circ\text{C}$ with occasional stirring until no free liquid remained. After removal of free solvent, the paste was allowed to rest (age) for 30 min with intermittent mixing to prevent crusting. The material was then dried at 80°C for 2 h and further dried at 110°C overnight. Finally, the dried impregnated carbon was thermally treated at 300°C for 2 h under a nitrogen atmosphere (Fig.2). The resulting Fe-modified carbon materials were stored in a desiccator until further characterization. The sample codes MAC1, MAC2.5, and MAC5 were retained for consistency and sample identification; the numbers denote the nominal Fe loading used during synthesis and do not imply experimentally confirmed magnetic properties.

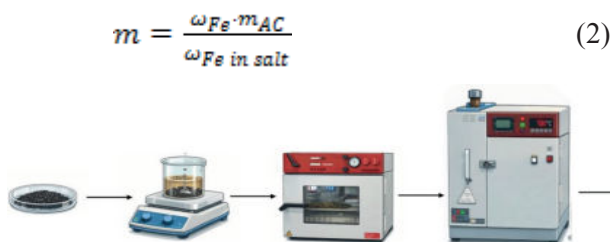


Figure 2. Scheme of the procedure to obtain the Fe-modified activated carbons.

MnFe₂O₄/Shymkent reference clay. The MnFe₂O₄/Shymkent reference clay used in this work was prepared according to the procedure described in our previous study (Zh. Baimuratova et al., 2024), in which the material was characterized separately.



Figure 3. Scheme of the procedure to obtain the MnFe₂O₄/Shymkent reference clay.

Batch experiments using Fe-modified activated carbons and the MnFe₂O₄/Shymkent reference clay. Batch adsorption experiments. Batch adsorption tests were performed using 100 mL of PCM or SMX solution at $C_0 = 50 \text{ mg} \cdot \text{L}^{-1}$ in 250 mL Erlenmeyer flasks. The material dose was $2.5 \text{ g} \cdot \text{L}^{-1}$, the initial pH was adjusted to 3.5 with 0.1 M HCl or NaOH, and the suspensions were agitated at 200 rpm and $60 \pm 1^\circ\text{C}$. These conditions were selected to enable direct comparison with the oxidation experiments; they should not be interpreted as optimized or representative of ambient wastewater treatment. The use of a single pH, temperature, and pollutant concentration is a limitation of the present study.

At 0, 5, 15, 30, 60, 120, 240, 480, 720, and 1440 min, 2 mL aliquots were withdrawn and filtered through $0.45 \mu\text{m}$ nylon syringe filters.

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (3)$$

where q_e is the adsorption capacity at the selected endpoint (mg g^{-1}), C_0 is the initial concentration of PCM or SMX (mg L^{-1}), C_e is the corresponding aqueous concentration of PCM or SMX (mg L^{-1}), V is the solution volume (L), and m is the mass of Fe-modified activated carbon or MnFe_2O_4 /Shymkent reference clay (g).

The adsorption concentration-time data were evaluated using the pseudo-first-order and pseudo-second-order kinetic models. Model performance was compared using the coefficient of determination (R^2), sum of squared errors (SSE), root mean square error (RMSE), and the agreement between calculated and experimental adsorption capacities. The model showing the higher R^2 together with lower SSE and RMSE values was considered the better empirical description of a given dataset. Kinetic-model agreement was not interpreted as direct proof of chemisorption.

Pseudo-first order model:

$$q_t = q_e \cdot (1 - e^{-k_1 t}) \quad (4)$$

Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (5)$$

where t is the contact time (min), q_t is the adsorption capacity at time t ($\text{mg} \cdot \text{g}^{-1}$), q_e is the adsorption capacity at equilibrium ($\text{mg} \cdot \text{g}^{-1}$), k_1 is the pseudo-first-order rate constant (min^{-1}), and k_2 is the pseudo-second-order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

SMX and PCM concentrations were quantified by HPLC using the following conditions: Inertsil ODS-3 column (250×4.6 mm, $5 \mu\text{m}$), mobile phase acetonitrile: ultrapure water (45:55, v/v) adjusted to pH 2.5, flow rate $1.0 \text{ mL} \cdot \text{min}^{-1}$, detection at 254 nm. The same HPLC analytical conditions were applied for the determination of SMX and PCM concentrations in all experiments described in this study.

Catalytic wet peroxide oxidation (CWPO, batch). CWPO experiments were conducted in 250 mL glass reactors containing 100 mL of PCM or SMX solution ($C_0 = 50 \text{ mg L}^{-1}$) and 0.25 g of material (2.5 g L^{-1}). The initial pH was adjusted to 3.5, and the reactors were maintained at $60 \pm 1^\circ\text{C}$ under agitation at 200 rpm. Hydrogen peroxide was used as the oxidant at an initial mass concentration of 44.3 mg L^{-1} (1.30 mmol L^{-1}). This oxidant dose was selected from the stoichiometric calculation for complete mineralization of SMX and was subsequently used as the fixed H_2O_2 concentration in the comparative oxidation experiments.

The stoichiometric calculation was based on the reaction $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S} + 33\text{H}_2\text{O}_2 \rightarrow 10\text{CO}_2 + 36\text{H}_2\text{O} + \text{H}_2\text{SO}_4 + 3\text{HNO}_3$. For an SMX concentration of 10 mg L^{-1} , the

amount of SMX is $3.948 \times 10^{-5} \text{ mol L}^{-1}$; therefore, 33 mol of H_2O_2 per mole of SMX corresponds to $1.302 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, or 44.3 mg L^{-1} . Using a 30% H_2O_2 solution and the calculation applied in this study, this concentration corresponds to 148 μL of the H_2O_2 solution per litre of reaction solution.

Samples were collected at 0, 5, 15, 30, 60, 120, 240, 360, 480, and 1440 min. Immediately after sampling, the reaction was quenched with sodium thiosulfate to stop further oxidation. Samples were then filtered through 0.45 μm nylon syringe filters and analysed by HPLC under the conditions described above. Residual oxidant was monitored during the treatment.

Sodium persulfate-assisted treatment (SPS, batch). SPS-assisted experiments were performed under the same batch conditions used for CWPO: 100 mL of PCM or SMX solution ($C_0 = 50 \text{ mg L}^{-1}$), 0.25 g of material (2.5 g L^{-1}), pH 3.5, $60 \pm 1^\circ\text{C}$, and 200 rpm. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was used as the oxidant. For direct comparison with the H_2O_2 -based system, the initial mass concentration of $\text{Na}_2\text{S}_2\text{O}_8$ was set equal to that of H_2O_2 , namely 44.3 mg L^{-1} . This corresponds to 0.186 mmol $\text{L}^{-1} \text{ Na}_2\text{S}_2\text{O}_8$.

The required mass of $\text{Na}_2\text{S}_2\text{O}_8$ was calculated using $m = C \times V$. For a solution volume of 0.966 L, $44.3 \text{ mg L}^{-1} \times 0.966 \text{ L} = 42.79 \text{ mg Na}_2\text{S}_2\text{O}_8$. Accordingly, 42.79 mg of sodium persulfate was used to prepare 0.966 L of solution at the target oxidant concentration. The same initial mass concentration (44.3 mg L^{-1}) was therefore applied in the H_2O_2 and SPS systems to enable direct comparison under the selected experimental conditions.

For the batch experiments at $C_0 = 50 \text{ mg L}^{-1}$, the corresponding SPS-to-pollutant molar ratio was approximately 0.94 for SMX and 0.56 for PCM. Samples were collected at 0, 5, 15, 30, 60, 120, 240, 360, 480, and 1440 min, immediately quenched with sodium thiosulfate, filtered through 0.45 μm nylon syringe filters, and analysed by HPLC. Residual SPS was monitored during treatment.

Oxidant-only control experiments. Control experiments were conducted in the absence of any carbon or clay material to evaluate the contribution of the oxidants themselves under the selected reaction conditions. PCM and SMX solutions ($C_0 = 50 \text{ mg L}^{-1}$) were treated with either H_2O_2 or sodium persulfate at an initial oxidant concentration of 44.3 mg L^{-1} , pH 3.5, $60 \pm 1^\circ\text{C}$, and 200 rpm. Samples were collected at 0, 15, 30, 60, 120, 240, 360, 480, and 1440 min, immediately quenched with sodium thiosulfate, filtered through 0.45 μm nylon syringe filters, and analysed by HPLC using the same procedure as for the material-containing experiments. These controls were used to assess direct H_2O_2 action and the possible contribution of thermal SPS activation at 60°C .

All experiments were performed in triplicate, and the results are presented as the mean value $\pm$ standard deviation.

Results and Discussion. The N_2 -physisorption results for all carbon samples are summarized in Table 1. The BET surface area followed the order MAC2.5 ($532 \text{ m}^2 \text{ g}^{-1}$) > MAC1 ($510 \text{ m}^2 \text{ g}^{-1}$) > AC ($462 \text{ m}^2 \text{ g}^{-1}$) > MAC5 ($423 \text{ m}^2 \text{ g}^{-1}$). The reported total pore volume was $0.224 \text{ cm}^3 \text{ g}^{-1}$ for all four carbon samples, while the micropore volume remained nearly constant at $0.181\text{--}0.182 \text{ cm}^3 \text{ g}^{-1}$. The mesopore volume decreased

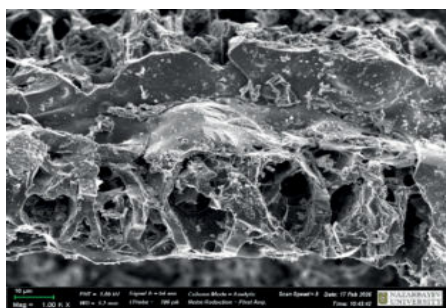
from $0.042 \text{ cm}^3 \text{ g}^{-1}$ for AC to 0.036, 0.033, and $0.030 \text{ cm}^3 \text{ g}^{-1}$ for MAC2.5, MAC1, and MAC5, respectively. The average pore diameter was $19.4 \text{ \AA}$ for AC, $16.8 \text{ \AA}$ for MAC2.5, $17.6 \text{ \AA}$ for MAC1, and $21.2 \text{ \AA}$ for MAC5. The non-monotonic variation in SBET with nominal Fe loading shows that increasing the amount of Fe precursor did not produce a proportional increase in accessible surface area. In particular, the lower SBET of MAC5 relative to MAC1 and MAC2.5 is consistent with reduced accessible surface at the highest nominal Fe loading, although the available physisorption data alone do not prove a specific pore-blocking mechanism. The highest SBET observed for MAC2.5 provides a textural basis for its consistently strong overall performance, while the comparison is interpreted cautiously because different analytical instruments and pretreatment procedures were used for at least part of the sample set.

Table 1. Textural properties of the synthesized activated carbons.

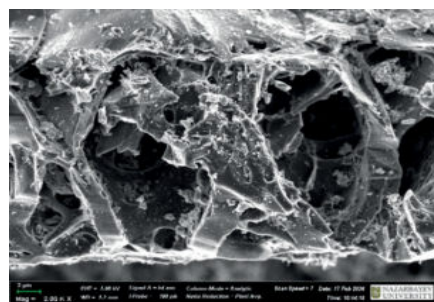
Material	SBET ($\text{m}^2 \text{ g}^{-1}$)	VTotal ($\text{cm}^3 \text{ g}^{-1}$)	Vmicro ($\text{cm}^3 \text{ g}^{-1}$)	Vmeso ($\text{cm}^3 \text{ g}^{-1}$)	Vmicro/ VTotal	dpore ($\text{\AA}$)
AC	462	0.224	0.182	0.042	0.81	19.4
MAC2.5	532	0.224	0.181	0.036	0.81	16.8
MAC5	423	0.224	0.181	0.030	0.80	21.2
MAC1	510	0.224	0.181	0.033	0.81	17.6
MnFe ₂ O ₄ /Shymkent*	74	1.77	—	—	—	—

*Zh. Baimuratova, et al., 2024.

Morphology and chemical composition (SEM–EDS analysis). SEM micrographs of MAC5, MAC2.5, and MAC1 showed that the channel-like morphology inherited from the corn-cob precursor remained visible after impregnation and thermal treatment (Figs. 4–6). EDS spectra and elemental maps confirmed the local presence and spatial distribution of Fe-containing regions on the analysed surfaces. Because SEM–EDS is a local and semi-quantitative technique, the EDS values are interpreted as indicative surface compositions and are not used as measurements of bulk Fe loading or as evidence of magnetic properties. Accordingly, the designations MAC1, MAC2.5, and MAC5 refer to nominal Fe loadings used during synthesis. The chemical form and crystalline phase of the incorporated Fe were not determined by phase-specific techniques in the present study; therefore, no assignment to a particular Fe oxide phase is made.



(a)

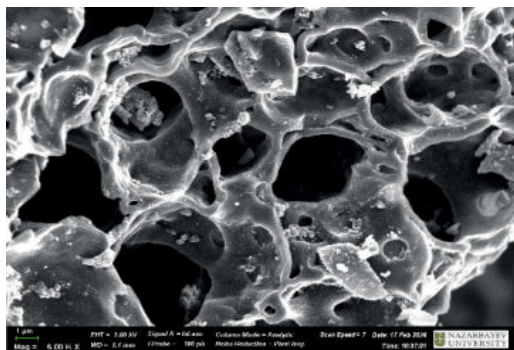


(b)

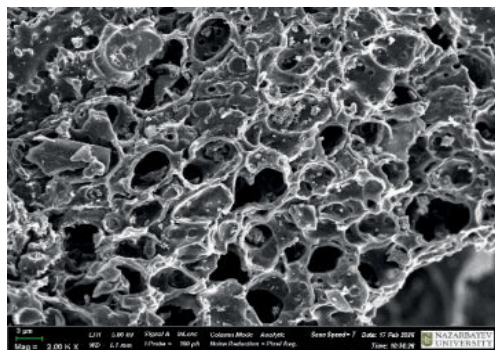
(c)

(d)

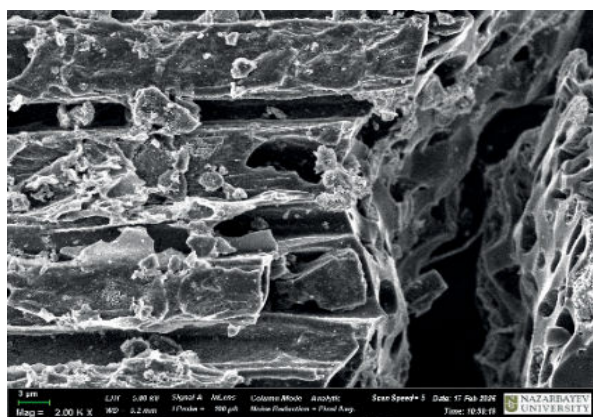
(e)



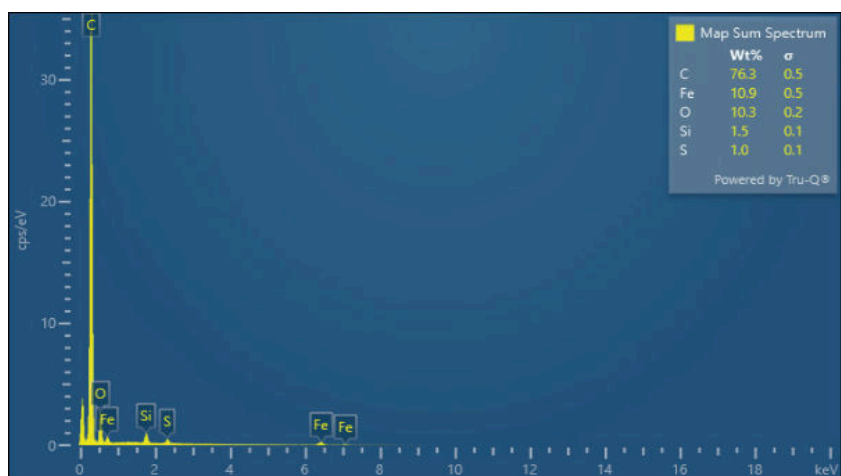
(a)



(b)



(c)



(d)

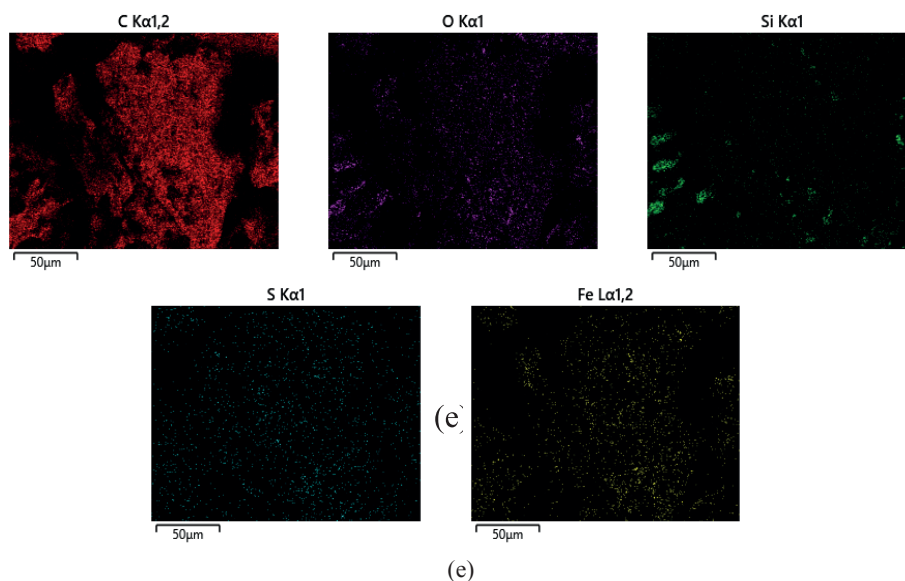
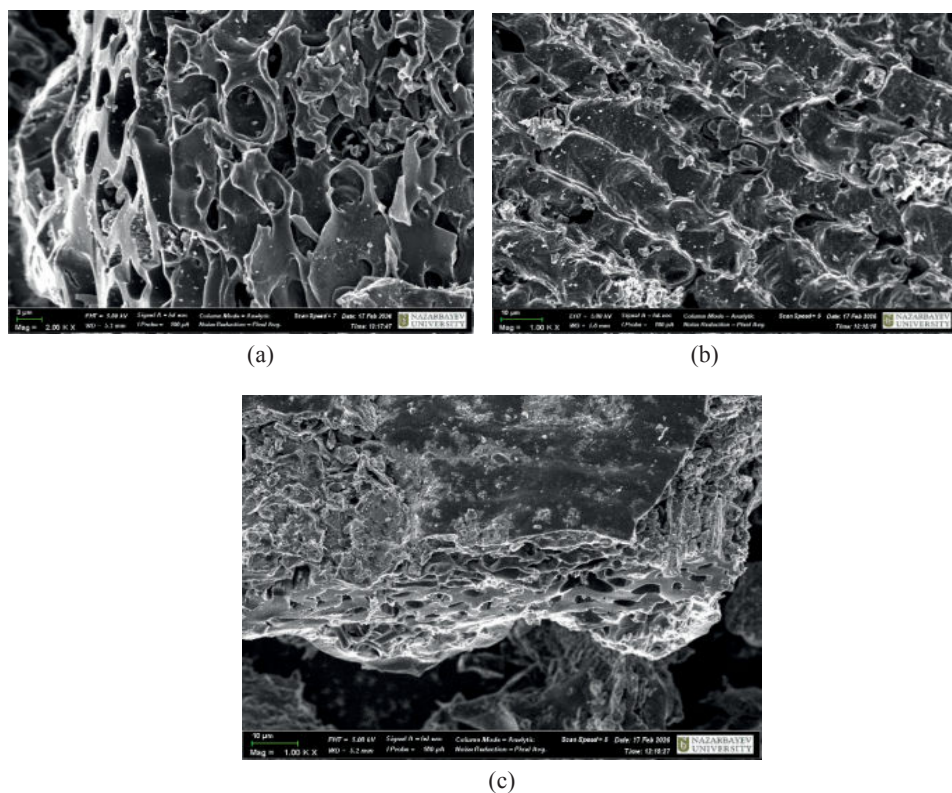


Figure 5. SEM micrographs of MAC2.5 ((a), (b), (c)), EDS spectrum of MAC2.5 (d), maps showing the distribution of C, O, Si, S and Fe of MAC2.5 (e).



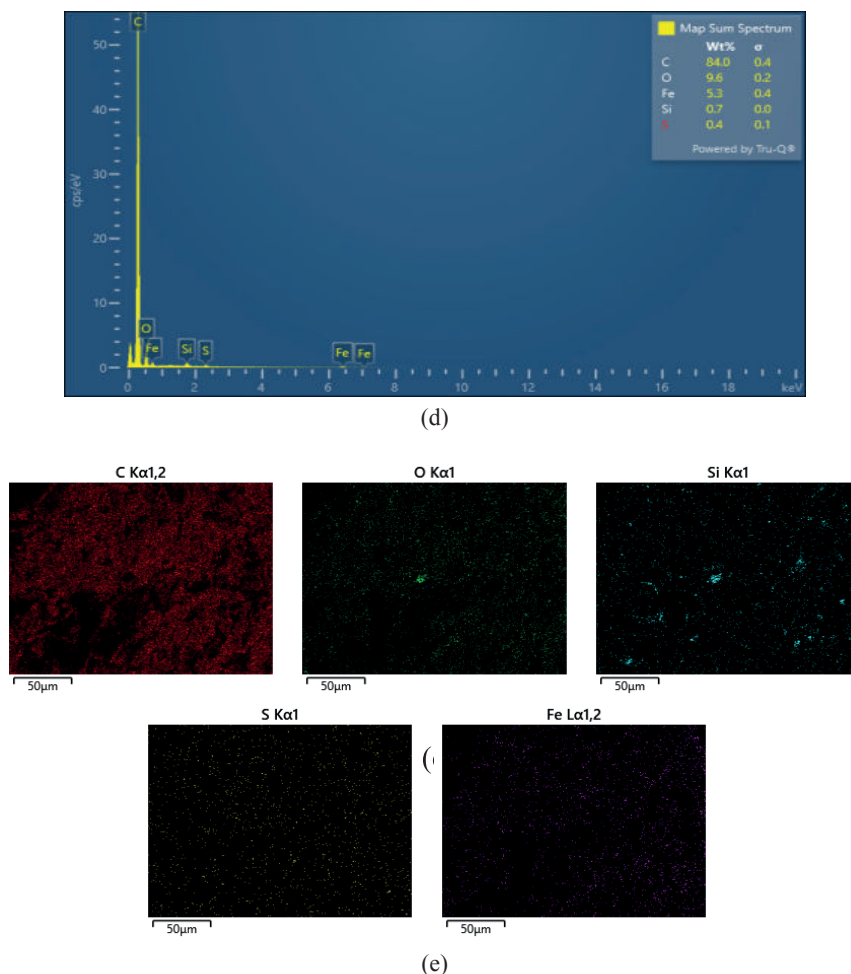


Figure 6. SEM micrographs of MAC1 ((a), (b), (c)), EDS spectrum of MAC1 (d), maps showing the distribution of C, O, Si, S and Fe of MAC1 (e).

Elemental analysis. Table 2 shows the results of elemental analysis of the synthesized materials, revealing that after activation and carbonization there is a sharp increase in the carbon content of the sample, the carbon content in AC reaches 76.08% by mass, whereas in the raw material (corn cob) it is only 12.08% by mass. At the same time, the nitrogen content increases from 0.62 to 1.93 wt.% and the hydrogen content from 1.57 to 2.60 wt.%, indicating the preservation and/or formation of surface heteroatom-containing functional groups in the activated carbon structure. The sulphur content remains at a very low level, amounting to 0.06 wt.% in AC, whereas it is not detected in the feedstock. Overall, the results of the CHNS analysis confirm the successful production of a carbonaceous material with a high degree of carbonization and the presence of a small amount of heteroatoms, which may be important for its adsorption and surface reaction properties.

In contrast, the previously reported MnFe₂O₄/Shymkent material characterization (Baimuratova et al., 2024) exhibits a completely different elemental composition, being dominated by oxygen (36.19 wt.%), silicon (25.71 wt.%), manganese (10.83 wt.%), and iron (15.04 wt.%), which reflects its inorganic oxide nature rather than a carbon-rich structure. This comparison clearly highlights the fundamental difference between AC and the MnFe₂O₄/Shymkent reference material in terms of elemental composition and expected surface chemistry.

Table 2. Elemental analysis of the synthesized materials.

Material	N (wt.%)	C (wt.%)	H (wt.%)	S (wt.%)
Raw material (corn cob)	0,62	12,08	1,6	0
AC	1,93	76,08	2,6	0,06
	O (wt.%)	Si (wt.%)	Mn (wt.%)	Fe (wt.%)
MnFe ₂ O ₄ /Shymkent*	36.19	25.71	10.83	15.04

*Zh. Baimuratova et al., 2024.

TGA analysis. Thermogravimetric analysis shows that the activated carbon AC exhibits high thermal stability, with only minor mass losses observed up to 700 °C (See Fig.7). The initial mass decrease is mainly associated with the removal of adsorbed moisture and volatile components, whereas the subsequent TG profile remains relatively stable, indicating the absence of intense decomposition processes and confirming the high degree of carbonization of the material (Kurtebayeva et al., 2026). In contrast, the material MnFe₂O₄/Shymkent reported by Baimuratova et al., 2024 displays a more complex thermal behavior, with several distinct weight-loss stages attributed to the dehydration of montmorillonite, hydromica, and kaolinite, as well as to the release of structural hydroxyl groups. The DTA and DTG curves of MnFe₂O₄/Shymkent show higher peak intensities than those of the natural clay, indicating a greater contribution of finely dispersed clay minerals and bound water. In addition, the increased mass loss in the modified clay reflects the higher content of dehydrating mineral phases, while the amount of thermally inert components such as quartz remains limited.

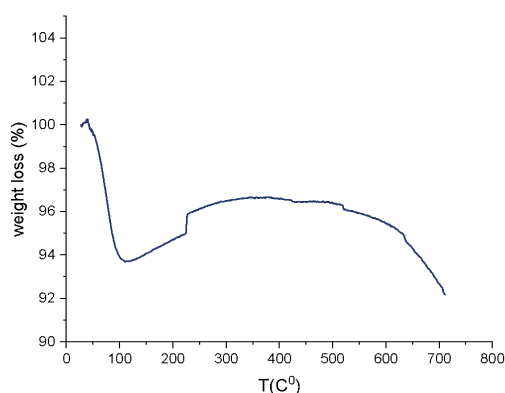


Figure 7. TG profile of AC.

Yield of activated carbon obtained. During the carbonization and activation of the raw material derived from corn cobs, the sample mass decreased significantly, 2.11 g of activated carbon being obtained from 7.58 g of raw material. This corresponds to a mass loss of approximately 72.2% and to a carbon yield of around 27.8%. The significant mass loss is due to the removal of moisture and volatile components, as well as to the thermal decomposition of the main structural components of the plant raw material, such as hemicellulose, cellulose and lignin (Neme et al., 2022). The yield obtained is typical of carbon materials synthesized from lignocellulosic raw materials and indicates the formation of a porous carbon matrix. Despite significant mass loss, the AC sample is characterized by a well-developed texture and high specific surface area, indicating the effectiveness of the chosen method to produce activated carbon.

Point of zero charge. Fig. 8 shows the results obtained by the pH drift method for the determination of the point of zero charge of the obtained materials. For all materials, the final pH value changes much less significantly than the initial pH value, indicating pronounced buffering properties of the surface and the system's tendency to reach equilibrium within a narrow pH range. For samples MAC5, MAC2.5, and MAC1, the final pH stabilizes in most cases in the range of approximately 5.5–6.2, whereas for $\text{MnFe}_2\text{O}_4/\text{Shymkent}$, a higher final pH is observed, especially at alkaline initial values, which may indicate differences in the composition of surface functional groups and the acid-base properties of the material.

The point where the curve intersects the line $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ can be used to estimate the point of zero charge (pH_{pzc}). Based on the presented data, the pH_{pzc} for the studied materials is likely in the neutral to slightly acidic range, approximately 5.8–6.2. This means that at $\text{pH} < \text{pH}_{\text{pzc}}$, the sorbent surface will be predominantly protonated and may interact better with anionic forms of pollutants, whereas at $\text{pH} > \text{pH}_{\text{pzc}}$, the surface acquires a negative charge and becomes more favorable for the adsorption of cationic particles (Yağmur, H., and Kaya, I. 2021). For $\text{MnFe}_2\text{O}_4/\text{Shymkent}$, a more pronounced deviation of the final pH toward the alkaline region may indicate greater surface buffering capacity or the involvement of hydroxyl groups in acid-base equilibria. Overall, the results obtained show that the acidity of the medium is an important factor determining the surface charge and, consequently, the adsorption efficiency.

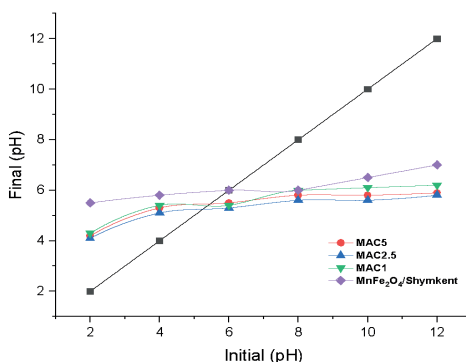


Figure 8. pH_{pzc} values of the obtained materials.

Comparative assessment of adsorption and oxidant-assisted performance of Fe-modified activated carbons and the MnFe₂O₄/Shymkent reference clay. Kinetic modeling of the adsorption process of contaminants of concern. As shown in Fig. 9, all of the studied materials exhibited a rapid initial uptake followed by a slower adsorption stage. This two-stage profile is consistent with the rapid occupation of readily accessible surface sites at the beginning of the experiment, followed by progressively slower transport toward less accessible adsorption sites and pores. The kinetic behavior was nevertheless strongly dependent on the adsorbent-pollutant pair. For PCM, the Fe-modified carbons showed a pronounced increase during the first several hours, while MnFe₂O₄/Shymkent continued to gain adsorption capacity over the longer contact period. For SMX, MAC2.5 and MAC1 also continued to increase between 480 and 1440 min, whereas MAC5 changed only slightly after the initial adsorption stage. Accordingly, the profiles are more accurately described as approaching a quasi-equilibrium over the 24 h experiment rather than reaching a common equilibrium time at 8 h. A similar combination of rapid surface uptake and a slower diffusion-controlled stage has been reported for pharmaceutical adsorption on porous carbonaceous adsorbents (Baghdadi et al., 2016; Álvarez-Torrellas et al., 2017).

Under the tested conditions, PCM showed substantially higher adsorption than SMX on all materials. The highest 24 h experimental uptake of PCM was obtained with MAC5 (17.08 mg g⁻¹), followed closely by MAC1 (16.31 mg g⁻¹) and MAC2.5 (16.20 mg g⁻¹), whereas MnFe₂O₄/Shymkent reached 13.19 mg g⁻¹. For SMX, MAC2.5 displayed the highest experimental uptake (7.52 mg g⁻¹), followed by MAC1 (5.18 mg g⁻¹), MAC5 (3.59 mg g⁻¹), and MnFe₂O₄/Shymkent (0.94 mg g⁻¹). These values represent adsorption capacities obtained at the applied initial concentration and contact time rather than maximum adsorption capacities, because only one initial pollutant concentration was investigated. The particularly low SMX uptake on MnFe₂O₄/Shymkent is consistent with its much lower BET surface area (74 m² g⁻¹) compared with the carbon materials, whereas the different ranking of the MAC samples shows that adsorption is governed not only by surface area but also by pore accessibility and surface chemistry.

The adsorption trends can also be interpreted in relation to the surface charge of the materials and the speciation of the pharmaceuticals. At the experimental pH of 3.5, which is below the estimated pH-zc range of approximately 5.8–6.2, the surfaces of the Fe-modified carbons are expected to be predominantly protonated (Yağmur and Kaya, 2021). Under these conditions, PCM and SMX are predominantly present in neutral molecular forms; therefore, the lower adsorption of SMX cannot be attributed to electrostatic repulsion between an anionic pollutant and a negatively charged carbon surface. Instead, adsorption on the carbon matrix is likely governed by a combination of pore filling, π - π interactions between the aromatic structures of the pharmaceuticals and the carbon surface, hydrogen bonding with surface functional groups, and dispersion interactions. Such simultaneous contributions are consistent with the complex adsorption behavior commonly observed for pharmaceutical compounds on activated carbons (Baghdadi et al., 2016; Álvarez-Torrellas et al., 2017). For

MnFe₂O₄/Shymkent, the low specific surface area and the distinctly inorganic surface chemistry limit the number and nature of adsorption sites available for SMX, despite its comparatively high total pore volume.

The kinetic parameters summarized in Table 3 further support the different adsorption behavior of the studied systems. For every adsorbent-pollutant pair, the pseudo-second-order model produced higher R² values and lower SSE and RMSE values than the pseudo-first-order model; the R² values increased from 0.7003–0.8893 for the pseudo-first-order fits to 0.8043–0.9579 for the pseudo-second-order fits. The calculated capacities from the pseudo-second-order model were also closer to the experimental values for most systems, indicating that this equation provides the better empirical description of the adsorption kinetics, in agreement with observations reported for pharmaceutical adsorption on magnetic carbonaceous adsorbents (Baghdadi et al., 2016). This statistical agreement does not, however, demonstrate a purely chemisorptive mechanism, because pore diffusion, physical adsorption and surface interactions can contribute simultaneously. The clearest deviation is observed for PCM adsorption on MnFe₂O₄/Shymkent, for which the pseudo-second-order fit gives $q_{cal} = 22.68 \text{ mg g}^{-1}$, exceeding the maximum solute inventory of 20 mg g^{-1} available under the applied experimental conditions. Thus, this individual fitted capacity represents an overestimation by the model and has no direct physical meaning, whereas the overall fitting statistics remain useful for comparing the shapes of the kinetic profiles.

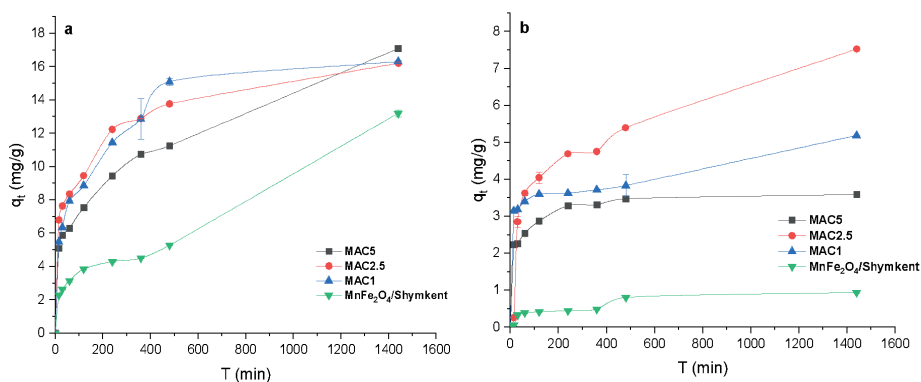


Figure 9. Kinetic adsorption curves for paracetamol (a) and sulfamethoxazole (b) with the Fe-modified activated carbons and the MnFe₂O₄/Shymkent reference clay.

Table 3. Kinetic parameters for SMX and PCM adsorption onto the Fe-modified activated carbons and the MnFe₂O₄/Shymkent reference clay.

	MAC5		MAC2.5		MAC1		MnFe ₂ O ₄ /Shymkent	
	PCM	SMX	PCM	SMX	PCM	SMX	PCM	SMX
q_{exp} (mg g ⁻¹)	17.08±0.1	3.59±0.04	16.20±0.01	7.52±0.01	16.31±0.01	5.18±0.03	13.19±0.1	0.94±0.01
Pseudo-first model								
q_{cal} (mg g ⁻¹)	12.58	3.21	13.13	5.67	13.96	3.86	16.11	0.88
k (min ⁻¹)	0.01	0.05	0.02	0.01	0.01	0.09	0.001	0.004

R ²	0.7003	0.8893	0.8083	0.8292	0.8454	0.8221	0.7955	0.7702
SSE	47.8741	0.9492	30.8601	6.8660	28.6591	2.3555	19.1364	0.1495
RMSE	2.6152	0.3682	2.0996	0.9904	2.0234	0.5800	1.6534	0.1461
Pseudo-second order								
q _{cal} (mg g ⁻¹)	14.70	3.42	14.45	6.73	15.64	4.06	22.68	0.94
k _{cal} (g mg ⁻¹ min ⁻¹)	8.32	0.04	0.002	0.002	0.001	0.04	3.8929	0.007
R ²	0.8201	0.9579	0.9075	0.8923	0.9268	0.8661	0.8043	0.8317
SSE	28.7346	0.3611	14.8909	4.3311	13.5600	1.7736	18.3117	0.1095
RMSE	2.0261	0.2271	1.4585	0.7866	1.3918	0.5034	1.6174	0.1250

Results of hydrogen-peroxide-assisted treatment. As shown in Fig. 10, hydrogen-peroxide-assisted treatment produced clearly different aqueous-phase removal profiles for PCM and SMX and also differentiated the Fe-modified carbons from the MnFe₂O₄/Shymkent reference. For PCM, the highest final removal was obtained with MAC2.5 and MAC1, reaching approximately 74% after 1440 min, while MAC5 reached about 57% and MnFe₂O₄/Shymkent about 32%. For SMX, the overall response was lower: MAC2.5 reached approximately 40%, followed by MAC1 at about 34%, MAC5 at about 28%, and MnFe₂O₄/Shymkent at about 23%. The higher performance of the Fe-modified carbon materials, particularly for PCM, is consistent with the combined role of a porous adsorptive carbon matrix and Fe-containing surface regions capable of promoting H₂O₂ activation. Fe-containing carbon materials are widely reported to promote Fenton-like reactions through Fe redox cycling, while adsorption on the carbon support can increase the local concentration of organic molecules near reactive surface sites (Esteves et al., 2024). Because the measured response is based on the decrease in parent-compound concentration, the values in Fig. 10 are interpreted as aqueous-phase removal arising from the combined effects of adsorption and oxidative transformation.

An oxidant-only control performed under otherwise identical conditions showed only limited parent-compound removal in the absence of the solid material. After 1440 min, H₂O₂ alone resulted in 12% removal of PCM and 6% removal of SMX. The low control values compared with the material-containing systems indicate that direct H₂O₂ action under the selected conditions accounts for only a minor fraction of the observed removal. The substantially higher values obtained with the Fe-modified carbons therefore support an additional contribution from the solid material, while the measured decrease in parent-compound concentration still represents the combined effects of adsorption and oxidative transformation rather than oxidation alone.

The different response of PCM and SMX cannot be explained by the electrostatic mechanism proposed previously. At pH 3.5, the Fe-modified carbon surfaces are expected to be positively charged because the working pH is below pH_{zc}, while both pollutants are predominantly neutral. The greater PCM removal therefore indicates more favorable overall interaction with the adsorbent-catalyst surface and/or higher susceptibility to oxidation under the applied conditions. Pore accessibility, π - π interactions, hydrogen bonding and adsorption affinity can facilitate transport of the pollutant toward Fe-containing regions, where H₂O₂ activation may occur. The lower

performance of $\text{MnFe}_2\text{O}_4/\text{Shymkent}$, despite its high total pore volume, is consistent with its much lower BET surface area and the predominance of a mineral pore structure, which provides a smaller accessible interfacial area than the microporous carbon matrix. The observed behavior therefore supports a coupled adsorption-oxidation process in which the carbon phase concentrates the pollutants near Fe-containing surface sites and Fe-mediated activation of H_2O_2 contributes to their subsequent removal (Esteves et al., 2024).

Among the Fe-modified carbons, MAC2.5 showed the most consistent performance, giving the highest SMX removal and a PCM removal essentially comparable to MAC1. Importantly, increasing the nominal Fe loading from 2.5 to 5 wt.% did not lead to a further improvement; MAC5 showed lower removal for both pollutants. The newly available textural data provide additional support for this non-monotonic response: MAC2.5 exhibited the highest SBET ($532 \text{ m}^2 \text{ g}^{-1}$), followed by MAC1 ($510 \text{ m}^2 \text{ g}^{-1}$), whereas MAC5 had the lowest SBET among the Fe-modified carbons ($423 \text{ m}^2 \text{ g}^{-1}$). Thus, the intermediate Fe loading combines the highest measured accessible surface area with Fe-containing surface regions, whereas the highest nominal Fe loading is accompanied by a decrease in accessible surface area. This trend is consistent with partial loss of accessible carbon surface at higher metal loading, as reported for Fe-loaded carbons (Esteves et al., 2024; Pereira et al., 2020), although the present data do not by themselves establish a specific pore-blocking mechanism.

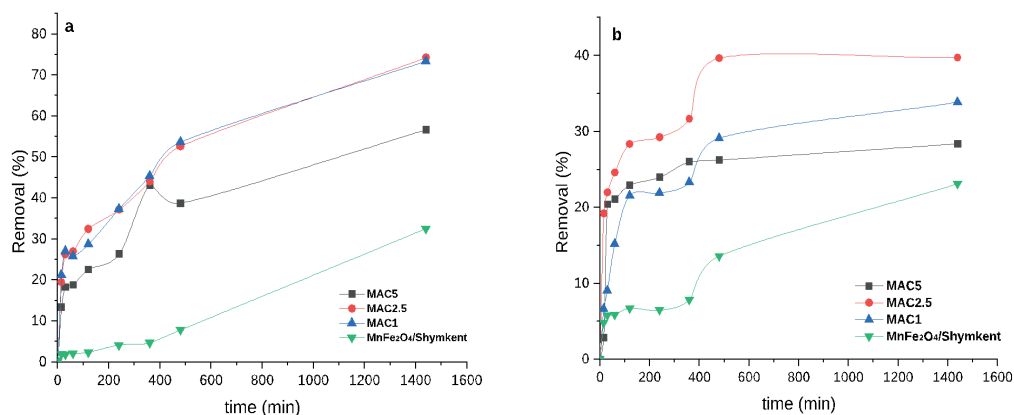


Figure 10. Aqueous-phase removal kinetics of (a) paracetamol and (b) sulfamethoxazole during hydrogen-peroxide-assisted treatment (CWPO conditions) with MAC5, MAC2.5, MAC1 and $\text{MnFe}_2\text{O}_4/\text{Shymkent}$ materials.

Results of SPS-assisted treatment. SPS-assisted treatment produced a markedly stronger decrease in the aqueous concentration of both pharmaceuticals than the hydrogen-peroxide-assisted system under the selected conditions (Fig. 11). For PCM, all tested solids showed an extremely rapid response, with removal already above approximately 95% at the first sampling stages and exceeding 98% by the end of the experiment. For SMX, the initial removal was also rapid but the final values were

lower, reaching approximately 70–74% for the Fe-modified carbons and about 50% for MnFe_2O_4 /Shymkent. The near-complete PCM removal observed not only for the MAC samples but also for the clay reference indicates that the response cannot be attributed exclusively to the specific textural properties of the Fe-modified carbons. At 60 °C, persulfate activation can be promoted thermally, while Fe-containing phases and carbon surfaces can additionally facilitate SPS activation through Fe redox cycling and surface electron-transfer processes (Wang and Wang, 2018; Pang et al., 2019; Tian et al., 2022). The observed profiles are therefore consistent with a combined contribution of adsorption, thermally promoted SPS activation, and heterogeneous reactions at Fe-containing surfaces.

The possible contribution of thermal SPS activation at 60 °C was evaluated directly using an oxidant-only control without carbon or clay material. In this control, PCM removal increased to only 13% and SMX removal to 7% after 1440 min. These results confirm that SPS can undergo a limited degree of thermally promoted activation under the applied conditions; however, thermal activation alone cannot account for the much higher removal observed in the presence of the Fe-modified carbons (>98% for PCM and approximately 70–74% for SMX). The control therefore supports an additional material-assisted contribution to SPS activation and/or pollutant removal, superimposed on adsorption and the thermal SPS background.

The particularly high PCM removal demonstrates the strong oxidative performance of the SPS system under the applied dosing basis. Both oxidants were used at the same mass concentration of 44.3 mg L⁻¹, although their molar concentrations were different (0.186 mmol L⁻¹ $\text{Na}_2\text{S}_2\text{O}_8$ versus 1.30 mmol L⁻¹ H_2O_2); consequently, the comparison reflects the performance of the two systems at equal oxidant mass concentration rather than at equal molar dose. Despite the lower molar concentration of SPS, the PCM concentration decreased almost completely, whereas the maximum PCM removal in the H_2O_2 system was approximately 74%. This behavior is consistent with the high reactivity of activated persulfate systems reported for Fe/carbon catalysts. The literature describes sulfate-radical and hydroxyl-radical pathways as well as non-radical electron-transfer routes during persulfate activation, with the carbon matrix participating in adsorption and electron transfer and Fe-containing sites promoting oxidant activation (Pang et al., 2019; Tian et al., 2022). In the present experiments, the reactive species were not identified directly; therefore, the exceptionally high PCM removal is interpreted as the overall response of the SPS-containing system rather than evidence for one specific radical pathway.

SMX displayed a different response from PCM. Although the Fe-modified carbons achieved approximately 70–74% removal after 24 h, the values remained clearly below the almost quantitative removal of PCM, while MnFe_2O_4 /Shymkent reached only about 50%. At pH 3.5, SMX is predominantly neutral and the catalyst surfaces are expected to be positively charged; consequently, the lower SMX response is not consistent with electrostatic repulsion of anionic SMX from a negatively charged surface. Instead, the difference points to pollutant-specific adsorption and oxidation behavior, including differences in molecular structure, adsorption orientation, accessibility to the Fe-

containing surface regions and susceptibility to the reactive species generated during SPS activation. Studies of Fe-containing carbon catalysts have shown that persulfate oxidation may involve both radical and non-radical pathways and that the relative contribution of these routes depends strongly on catalyst structure and pollutant chemistry (Pang et al., 2019; Tian et al., 2022; Qin et al., 2024). The similar final values obtained for MAC1, MAC2.5 and MAC5 in the SPS system also indicate that, once SPS activation becomes dominant, increasing the nominal Fe loading beyond the intermediate level provides only a limited additional benefit.

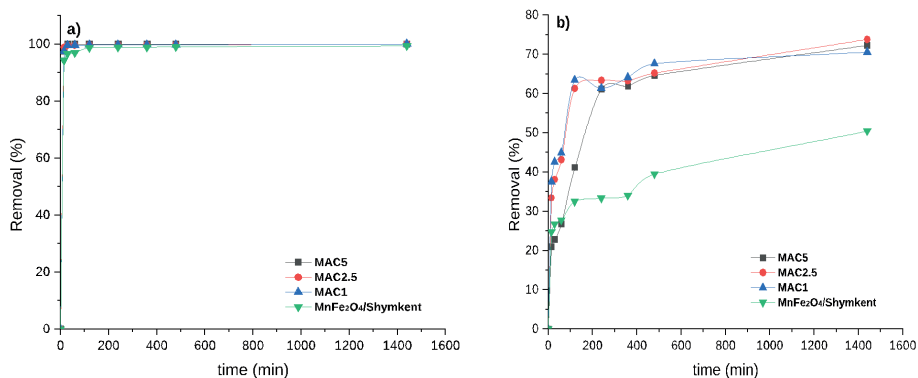


Figure 11. Aqueous-phase removal kinetics of (a) paracetamol and (b) sulfamethoxazole during sodium persulfate-assisted treatment (SPS) with MAC5, MAC2.5, MAC1 and MnFe₂O₄/Shymkent materials.

Overall, the comparison of the two oxidant systems demonstrates that SPS-assisted treatment provided the strongest aqueous-phase removal under the tested model-water conditions. The oxidant-only controls showed that H₂O₂ alone produced only 12% PCM and 6% SMX removal after 24 h, while SPS alone at 60 °C produced 13% PCM and 7% SMX removal. Thus, direct oxidant action and thermal SPS activation contributed only modestly to parent-compound disappearance relative to the material-containing systems. The advantage of SPS was especially pronounced for PCM, for which removal exceeded 98% with the Fe-modified carbons, whereas the best H₂O₂-assisted removal was approximately 74%. For SMX, the Fe-modified carbons reached approximately 70–74% removal in the SPS system. Across adsorption and both oxidant-assisted systems, MAC2.5 displayed the most consistently high overall performance. This behavior is now supported by the textural data, since MAC2.5 had the highest measured S_{BET} (532 m² g⁻¹), compared with 510 m² g⁻¹ for MAC1 and 423 m² g⁻¹ for MAC5, suggesting that the intermediate nominal Fe loading provides a favorable compromise between accessible carbon surface and Fe-containing functionality. The comparison is specific to the applied equal-mass oxidant dose and demonstrates enhanced parent-compound removal; it does not by itself establish complete mineralization of PCM or SMX.

Conclusions. Corn-cob-derived activated carbon was successfully functionalized with nominal Fe loadings of 1, 2.5, and 5 wt.% and evaluated for adsorption and oxidant-

assisted removal of PCM and SMX. SEM–EDS confirmed Fe-containing regions on the carbon surfaces, but, because this technique is local and semi-quantitative, the sample codes are treated as nominal Fe-loading designations rather than measured bulk Fe contents. Magnetic properties were not directly measured in the present study; therefore, the synthesized carbon samples are consistently described as Fe-modified activated carbons. N₂-physisorption showed SBET values of 510, 532, and 423 m² g⁻¹ for MAC1, MAC2.5, and MAC5, respectively, compared with 462 m² g⁻¹ for AC. The highest accessible surface area was therefore observed for MAC2.5, whereas the decrease for MAC5 indicates that increasing the nominal Fe loading does not monotonically improve the porous characteristics.

Adsorption was strongly pollutant- and material-dependent, with the highest 24 h experimental uptake reaching 17.08 mg g⁻¹ for PCM on MAC5 and 7.52 mg g⁻¹ for SMX on MAC2.5. The pseudo-second-order equation provided the best empirical description of the kinetic datasets according to R², SSE, and RMSE, although this statistical fit was not taken as proof of a single chemisorption mechanism. During hydrogen-peroxide-assisted treatment, MAC2.5 and MAC1 showed the highest PCM removal (approximately 74%), while MAC2.5 also gave the strongest SMX response (approximately 40%). The H₂O₂-only control produced only 12% PCM and 6% SMX removal after 24 h. SPS-assisted treatment was substantially more effective, producing >98% PCM removal and approximately 70–74% SMX removal for the Fe-modified carbons; the corresponding SPS-only control reached only 13% and 7%, respectively. These control experiments demonstrate that direct oxidant action and thermal SPS activation contribute to the process but are insufficient to explain the much higher removal achieved in the presence of the Fe-modified carbons. At pH 3.5, the carbon surfaces are expected to be protonated and both pharmaceuticals predominantly neutral, so the observed differences are better explained by pore accessibility, adsorption affinity, pollutant-specific reactivity and Fe-mediated oxidant activation than by electrostatic repulsion. Overall, MAC2.5 provided the most consistent performance across the tested systems, in agreement with its highest measured SBET while the observed parent-compound disappearance should not be interpreted as confirmed mineralization.

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