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Removal of organic pollutants – mycotoxin ochratoxin A and pharmaceutical ketoprofen by cationic surfactant modified kaolinite

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ABSTRACT

The potential of kaolin modified with a cationic surfactant - hexadecyltrimethylammonium (HDTMA) bromide as an adsorbent for the removal of two different contaminants: mycotoxin - ochratoxin A (OCHRA) and the pharmaceutical - ketoprofen (KET) from buffer solutions (pH 7) was investigated. The amount of HDTMA used for modification was equal to 50% of kaolin's cation exchange capacity (CEC). The obtained material (HKR-50) was characterized using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry/thermogravimetric analysis (DSC/TG), and scanning electron microscopy (SEM), confirming successful surface modification of kaolinite with HDTMA. Adsorption experiments demonstrated that HKR-50 exhibited significantly enhanced removal efficiency for both OCHRA and KET compared to unmodified kaolin. Nonlinear adsorption isotherms suggested a complex mechanism involving both hydrophobic and electrostatic interactions between contaminants and HDTMA ions. The data fit well to the Langmuir model, with maximum adsorption capacities of 2.57 mg/g for OCHRA and 1.40 mg/g for KET. These findings indicate that surfactant-modified kaolin is a promising and cost-effective adsorbent for the removal of mycotoxins from animal feed and pharmaceuticals from contaminated water, contributing to environmental protection and public health.

Keywords: kaolin, surfactant, ochratoxin A, ketoprofen, adsorption.

1. Introduction

Kaolin is a naturally occurring raw material widely used across various industries due to its adsorptive properties. Usually, in kaolin samples, kaolinite was identified as the main mineral, with quartz, muscovite, calcite or mica as impurities (Lopes et al. 2024). The aluminosilicate nature of kaolin exhibits high surface activity and the capacity to adsorb various substances. However, due to its low cation exchange capacity (CEC) and hydrophilic surface, natural kaolin often has limited efficiency in adsorbing low polar contaminants. This limitation can be overcome by modifying kaolin with surfactants, enhancing its adsorptive capabilities and expanding its potential applications, particularly in the fields of environmental protection and public health (Obradović et al. 2022; M. Spasojević et al. 2021).

Mycotoxins are toxic secondary metabolites produced by fungi that can contaminate various agricultural products, including grains, animal feed, nuts, and dried fruits (M. Spasojević et al. 2021). One of the most prominent mycotoxins is ochratoxin A – OCHRA (Table 1), which is commonly found in animal feed and represents a significant risk to animal and human health. OCHRA has been associated with various health issues, including kidney damage, immune system dysfunction, and potential carcinogenicity (Mannaa and Kim 2017; Spasojević et al. 2019).

On the other hand, pharmaceutical drugs such as ketoprofen – KET (Table 1), a nonsteroidal anti-inflammatory drug (NSAID), often contaminate water systems due to improper disposal and waste (Mansouri et al. 2024). Ketoprofen is widely used to treat pain and inflammation, but its presence in water bodies is considered as a risk to aquatic organisms and humans, as it can disrupt biological processes, causing toxicity and ecological imbalances (Lakshmi et al. 2024).

Developing effective methods to remove mycotoxins from contaminated feed as well as NSAIDs from polluted water has become increasingly critical in the context of environmental protection and public health. The adsorption is one of the most effective ways for the removal of both mycotoxins and pharmaceuticals. Surfactant-modified kaolin, such as with quaternary ammonium salts (hexadecyltrimethylammonium - HDTMA bromide), has shown significant potential in this regard, as modification enhances its ability to effectively adsorb a wide range of contaminants, including mycotoxins and NSAIDs (Obradović et al.

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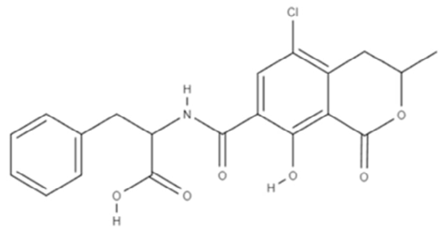
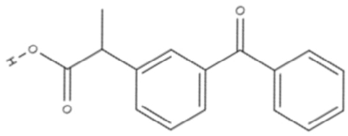
Table 1. Chemical structure and properties of OCHRA and KET (M. Spasojević et al. 2021; Cladière et al. 2018; Alagbe et al. 2022; Soto et al. 2020)

Chemical structure: OCHRA					
					
Molecular formula	CAS number	Molecular mass (g/mol)	Water solubility	pKa	logKow
$C_{20}H_{18}ClNO_6$	303-47-9	403.81	Low solubility	pK_{a1}=3.5 pK_{a2}= 7.0	4.74
Chemical structure: KET					
					
Molecular formula	CAS number	Molecular mass (g/mol)	Water solubility	pKa	logKow
$C_{16}H_{14}O_3$	22071-15-4	254.28	Low solubility	4.45	3.12

2022; M. Spasojević et al. 2021; Smiljanić et al. 2021; Marković et al. 2017).

This study presents the first comprehensive investigation of the removal of the mycotoxin ochratoxin A and the pharmaceutical ketoprofen using HDTMA-modified kaolin, including a detailed analysis of the adsorption behavior of both pollutants at pH 7. The obtained results highlight the potential of surfactant-modified kaolin as a cost-effective and versatile adsorbent for environmental and public health applications.

2. Materials and methods

The starting material for the experiments was natural kaolin from Rgotina, Serbia, which was modified by adding hexadecyltrimethylammonium (HDTMA) bromide. The modification process involved the use of HDTMA in an amount equivalent to 50% of kaolin's CEC, and the resulting material was denoted as HKR-50.

Adsorption of KET and OCHRA onto HKR-50 was followed by determination of adsorption isotherms. KET was tested at initial concentrations ranging from 2 to 20 mg/L, while OCHRA was tested with initial concentrations from 1 to 4.5 mg/L, both in 0.1 M phosphate buffer (pH 7), at fixed amount of adsorbent (10 mg/10 mL for KET and 2.5 mg/10 mL for OCHRA). After 30 min of shaking, suspensions were centrifuged, and the supernatants were analyzed by high-performance liquid chromatography (HPLC) using UV detection for KET (λ = 220 nm) and fluorescence detection for OCHRA (λ_{ex} = 365 nm and λ_{em} = 450 nm). The amount of KET and OCHRA adsorbed was calculated from the difference between the initial and final concentrations of investigated analyte in the supernatants.

The kaolin sample, before and after modification, was characterized by Fourier transformed infrared spectroscopy (FTIR), thermal analysis – diferential scanning calorimetry / thermogravimetry (DSC/TG) and scanning electron microscopy (SEM). FTIR spectroscopy was performed by using a Thermo Scientific Nicolet iS50 spectrophotometer. FTIR spectra were recorded using attenuated total reflection (ATR) with a diamond ATR smart accessory. Spectra were recorded in the range of 4000–400 cm^{-1} at 64 scans per spectrum at 2 cm^{-1} resolution. A background scan was acquired before scanning the samples. Thermal analysis was performed on a NETZSCH STA 449 F5 Jupiter. Samples were heated (25-1100 ºC) in a synthetic air atmosphere with a heating rate of 10 ºC/min. Before analysis, samples were dried at 60 °C for 2 h and kept in a desiccator at a relative humidity of 75% for 24 h. Electron micrographs were acquired using a JEOL JSM-7001F field emission scanning electron microscope, SEM (JEOL Ltd., Tokyo, Japan). The samples were coated with gold prior to the SEM analysis, producing a 15 nm thick electrically conductive coating.

3. Results and discussion

FTIR spectra of kaolin and HKR-50 are shown in Figure 1. FTIR spectra of the unmodified kaolin showed typical absorption bands associated with kaolinite, these bands did not change their shape or position in HKR-50, confirming that the structure of kaolin remained unchanged after modification with surfactant. Since the main characteristic bands of long chain organic cations at mineral surfaces are visible in the region from 3500 to 1400 cm^{-1}, this region was used for discussion of FTIR spectra of adsorbents. In the FTIR spectrum of HKR-50, new absorption bands were observed at 2925 and 2854 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations, and at 1468 cm^{-1}, corresponding to the bending vibrations of CH_2 groups - all originating from the alkyl chains of the quaternary ammonium surfactant (Obradović et al. 2022; M. Spasojević et al. 2021). The appearence of these bands compared to unmodified kaolin confirms successful surfactant loading on the kaolin surface. Moreover, slight shifts in the CH_2 stretching bands toward higher wavenumbers (from typical values around 2917 cm^{-1} and 2849 cm^{-1} for solid HDTMA (Kung and Hayes 1993) to 2925 and 2854 cm^{-1} in HKR-50) may suggest gauche conformations of the alkyl chains, indicating that the surfactant is adsorbed in less ordered arrangements of alkyl chains (Slaný, Jankovič, and Madejová 2019).

Thermal analysis (DSC/TG) was used to investigate the thermal behaviour of raw kaolin and surfactant-modified kaolin. The corresponding DSC (a) and TG (b) curves are shown in Figure 2.

Both kaolin and HKR-50 exhibit three characteristic thermal peaks typical of kaolinite. A broad, low-intensity endothermic peak below 180 °C is associated with dehydration, accompanied by mass losses of 0.55% for kaolin and 0.32% for HKR-50. This is followed by a more intense endothermic peak at 517 °C for kaolin and 515 °C for HKR-50, corresponding to dehydroxylation and the formation of metakaolin, with mass losses of 7.96% and 7.99%, respectively (Mitrović et al. 2009). Finally, a sharp exothermic peak at 990 °C (kaolin) and 992 °C (HKR-50) relates to the recrystallization of metakaolin, with no significant mass change at this region (Mitrović et al. 2009). Additionally, the DSC curve of HKR-50 exhibits an exothermic peak at 304 °C, attributed to oxidation of the surfactant on the kaolin surface. This process is accompanied by a higher mass loss in HKR-50 (1.48%) compared to raw kaolin (0.68%), which clearly indicates the presence of the surfactant in the surfactant-modified kaolin.

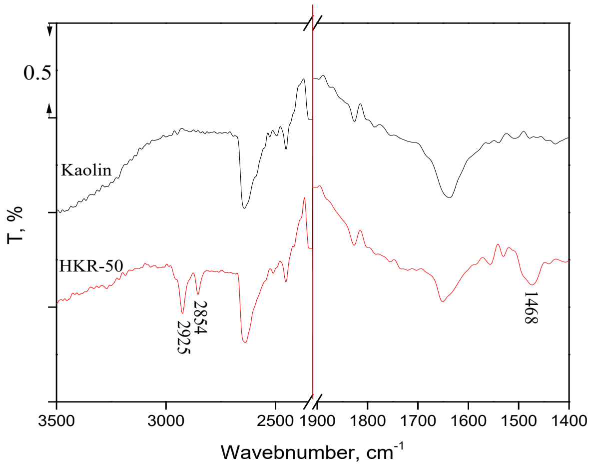


Fig. 1. FTIR spectra of Kaolin and HKR-50

The SEM micrographs of natural kaolin and surfactant-modified kaolin are shown in Figure 3. The natural kaolin exhibits a structure composed of stacked plates consisting of numerous layers, as commonly observed in kaolinite minerals (Figure 3a) (Werling et al. 2022). In the case of HKR-50, the layered structure of kaolinite remains unchanged. However, changes can be seen on the particle surfaces in the form of aggregates of HDTMA (red arrow Figure 3b), suggesting that HDTMA ions are randomly distributed over the external surfaces and edges of the kaolinite particles. FTIR spectroscopy, DSC/TG and SEM analysis confirmed the successful modification of kaolin with HDTMA ions.

In order to determine the mechanism of adsorption of KET and OCHRA on HKR-50, adsorption isotherms were determined and results are presented at Figure 4.

The adsorption of KET and OCHRA was studied at various initial concentrations at pH 7. The structures of the studied compounds indicate that they are hydrophobic molecules that contain ionizied functional groups - carboxylic group in KET and both carboxylic and phenolic groups in OCHRA. Based on their dissociation constants (Table 1) (pKa = 4.45 (carboxylic group) for KET; pKa_1 = 3.5 (carboxylic group) and pKa_2 = 7.0 (phenolic group) for OCHRA), both compounds are expected to be in an anionic form at pH 7. Natural kaolin, which possesses a negatively charged hydrophilic surface and hydrated inorganic cations, is generally inefficient in the removal of hydrophobic molecules (Duarte-Silva et al. 2014). Preliminary experiments confirmed that unmodified kaolin exhibits no significant affinity toward KET or OCHRA. Therefore, kaolin modified with a cationic surfactant due to the increased hydrophobicity significantly increased the adsorption of both contaminants. Results suggested that HDTMA ions present at the surface of kaolin represent active sites at which contaminants were adsorbed. As can be seen from Figure 4, adsorption of OCHRA and KET increased with increasing of the initial contaminants concentration. Nonlinear adsorption isotherms were obtained, and the experimental data were fitted using the Langmuir and Freundlich models. The corresponding adsorption parameters are summarized in Table 2.

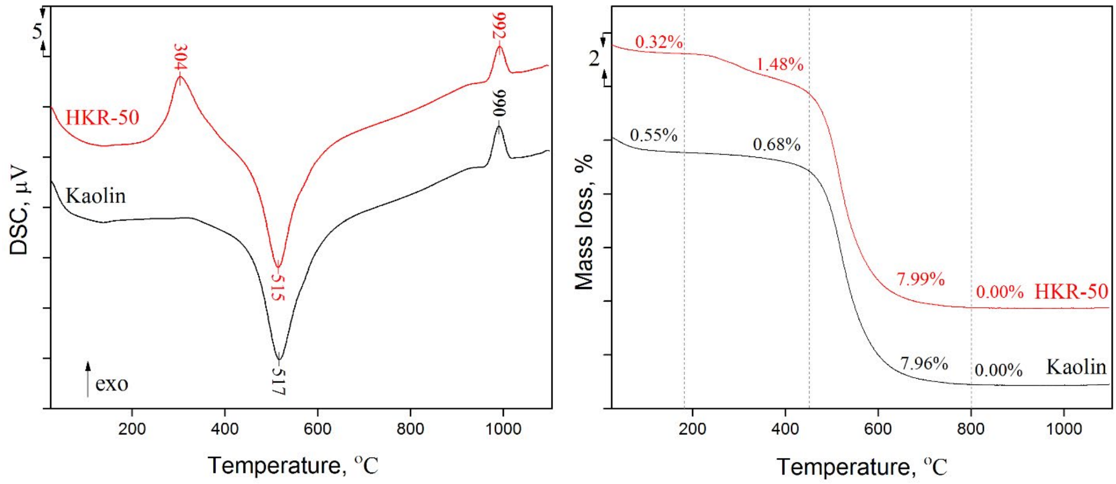


Fig. 2. DSC a) and TG b) curves of Kaolin and HKR-50

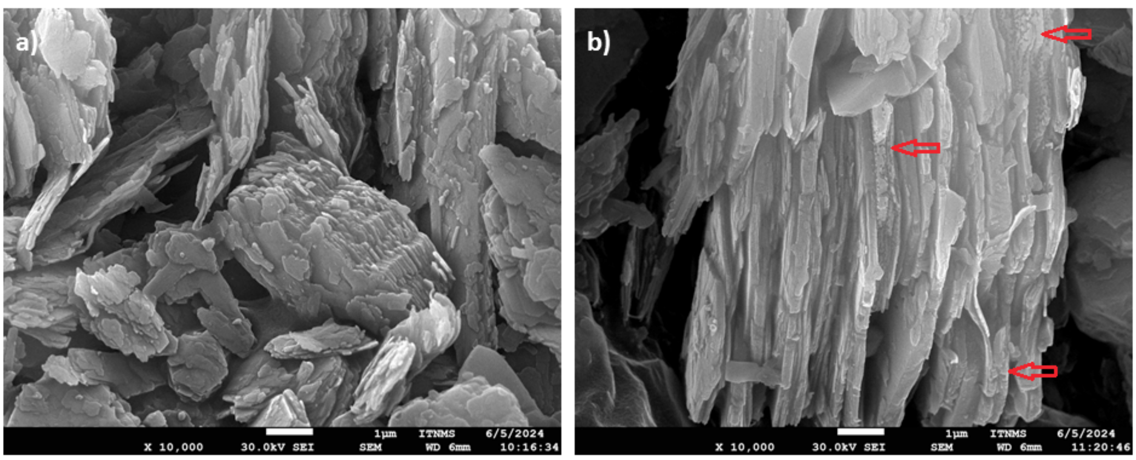


Fig. 3. SEM images: (a) Kaolin, (b) HKR-50

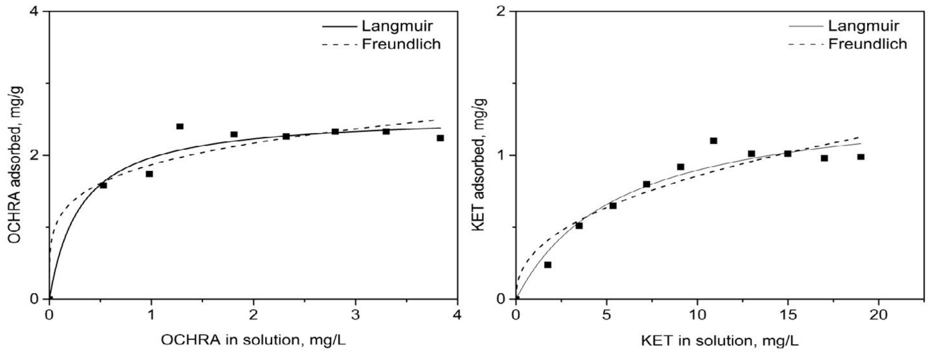


Fig. 4. Adsorption of OCHRA (Ožegović et al. 2025) and KET by HKR-50 at pH 7

Table 2. Calculated parameters of isotherm models for OCHRA (Ožegović et al. 2025) and KET adsorption

	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (L/mg)	r^2	n	K_F ($L^{1/n}$ $mg^{(1-1/n)}$ g^{-1})	r^2
OCHRA	2.57	3.278	0.955	4.648	1.870	0.911
KET	1.40	0.177	0.949	3.099	0.424	0.899

The correlation coefficient of the plots (r^2) demonstrated that both the Langmuir and Freundlich models well describe the adsorption of OCHRA and KET by surfactant-modified kaolin. A good fit of both Langmuir and Freundlich models indicates that the modified kaolin surface is partially heterogeneous, with some uniform active sites allowing monolayer adsorption and other active sites exhibiting varied binding energies. The Langmuir adsorption model for OCHRA had a maximum adsorption capacity (Q_m) of 2.57 mg/g with a high correlation coefficient (r^2 = 0.955), while KET adsorption was characterized by a Q_m value of 1.40 mg/g (r^2 = 0.949).

The obtained nonlinear isotherms suggest that the adsorption mechanism is complex and involves multiple types of interactions. Specifically, hydrophobic interactions occur between the hydrophobic regions of the contaminants (drug or mycotoxin) and the hydrophobic chains of the surfactant. In addition, since both KET and OCHRA are present in their anionic forms at pH 7, they interact electrostatically with the positively charged "heads" of the HDTMA molecules. The obtained results demonstrated that surfactant-modified kaolin exhibited enhanced adsorption for both KET and OCHRA, confirming that surfactant molecules are active sites responsible for the adsorption of both contaminants. Overall, the modified kaolin showed good affinity toward both contaminants, with notably better performance in the removal of OCHRA.

4. Conclusion

This study has shown that surfactant-modified kaolin, prepared with quaternary ammonium salt (HDTMA bromide), is an effective adsorbent for removing both ketoprofen and ochratoxin A from aqueous solutions. The modification process significantly enhanced kaolin's adsorption properties, with both contaminants being adsorbed more efficiently compared to unmodified kaolin. These findings suggest that surfactant-modified kaolin could be an effective adsorbent for the decontamination of animal feed and the removal of pharmaceuticals from water, addressing important environmental and public health concerns.

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