

Enhanced Interaction of Ciprofloxacin with Humic Substances and Magnetite-Silica-Nanoparticles in Multicomponent System: Spectrophotometric and Electrokinetic Studies

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Abstract. We evaluated the effect of dissolved organic matter (DOM) on the sorption of antibiotic ciprofloxacin (CIP) by magnetite-silica nanoparticles (NPs). For this purpose, magnetite NPs (M) modified with organosilanes (tetraethoxysilane and 3-aminopropyltriethoxysilane, TA) were used as a natural model of colloidal particles and a sorbent. Absorption spectra did not manifest any interaction between CIP and humic preparation (HP, sodium salt of humic acids) in aquatic system at pH from 6 to 8. On the contrary, the introduction of the MTA NPs into a bicomponent system of CIP incubated with HP lead to more than twice increased CIP sorption. Results of electrokinetic measurements in terms of zeta potential figured out the interaction mechanism in the CIP-HP-NPs system. In the three-component system, the MTA surface completely recharged from negative to positive, and importantly this effect is pH-dependent. The MTA zeta potential varied from –15 (pH 6) and –30 mV (pH 8) to +10 (pH 6) and +2 (pH 8). The study provides novel information on very actual topic in biomedical and ecological research since NPs are increasingly produced and implemented for various medical and environmental applications, including sorption of emerging ecotoxins (pharmaceuticals), but the assessment of naturally occurring DOM in water should not be ignored. © 2024 Journal of Biomedical Photonics & Engineering.

Keywords: antibiotic; colloidal particles; natural anionic polyelectrolytes; dissolved organic matter; sorption; zeta potential.

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1 Introduction

The pharmaceuticals are currently increasingly contributing to environmental pollution [1]. Over the past decade, the production of antibiotics has doubled [2, 3]. Chronic use of antibiotics can pose a significant environmental risk due to improper disposal of expired and unused drugs [4]. Accidental or deliberate entry of antibiotics into wastewater is a common phenomenon that radically affects both chemical and physical properties of natural water and the ecosystem as a whole [5]. The ciprofloxacin (CIP), a fluoroquinolone antibiotic, is a synthetic broad-spectrum antimicrobial agent. Fluoroquinolones are not destroyed completely in the body, and as a result are released into the environment in large quantities. Their presence in the environment can cause the development and spread of drug resistance in bacteria [6], creating potentially serious threats to human health and the ecosystem. CIP is among the top ten antibiotic contaminants [7] in surface water and hospital wastewater, where CIP concentrations reach $6.3 \cdot 10^{-4} \text{ mg} \cdot \text{L}^{-1}$ and $0.1245 \text{ mg} \cdot \text{L}^{-1}$ respectively [8].

Various sustainable remediation technologies have been developed to remove CIP from water, including photocatalytic degradation, advanced oxidation processes (AOPs), biodegradation, electrochemical processes, membrane separation, and adsorption [9] using different classes of adsorbents such as carbon nanotubes (CNTs), carbon nanofibers, biochar, biosorbents, metal-organic frameworks (MOFs), and nanocomposites. Among the purification methods used according recent publications [9–10], adsorption treatment has proved to be effective due to numerous advantages such as low cost, ease of operation, simple design, reusability, insensitivity to CIP [11], energy safety [12]. In addition, no intermediate by-products are formed during this purification [13]. So many adsorbents and nanomaterials, including polymers, zeolites, activated carbon, and carbon-based adsorbents [9] such as magnetic N-doped nanoporous carbon [9], and mesoporous silica [14, 15] have been studied as potential adsorbents of CIP from aqueous solutions under different experimental conditions. For example, ordered carbon exhibited a notable CIP removal capacity of $233.4 \text{ mg} \cdot \text{g}^{-1}$ under specific conditions [16], activated carbon derived from bamboo demonstrated $362.9 \text{ mg} \cdot \text{g}^{-1}$ [16]. The potential of nanomaterials like graphene oxide/sodium alginate was highlighted by achieving a $100.00 \text{ mg} \cdot \text{g}^{-1}$ removal under particular circumstances [17]. Other materials, such as bentonite [7], cationic flaxnoil cellulose, and biochar from tea leaves, have also exhibited varying levels of CIP removal [9]. Carbon-based adsorbents, such as magnetic N-doped nanoporous carbon, exhibit higher q_{max} ($1563.7 \text{ mg} \cdot \text{g}^{-1}$) than other adsorbents. However, the efficacy of adsorption is heavily reliant on factors such as cost, the physicochemical properties of the adsorbent, solution pH, and competing solutes [9], underscoring the need for tailored adsorption systems to achieve efficient CIP removal. Among adsorbents proposed above, magnetite mesoporous silica nanomaterials are promising due to

economical reason, the large specific surface area and porosity (to $300 \text{ m}^2 \cdot \text{g}^{-1}$) [18], regular channel structure [19], inert, biocompatible [20] and reusable due to their very high saturation magnetization [21, 22]. In addition, due to the power of highly reactive hydroxyl radicals ($\bullet\text{OH}$) to degrade recalcitrant organic compounds in Fenton processes the AOPs using Fe_3O_4 NPs not only break down the CIP's chemical structure but also lead to the formation of potentially less harmful degradation products.

When assessing the potential of a sorbent should be taken into account the presence of dissolved organic matter (DOM) in real water. It will result in reducing sorbent efficiency for CIP. Humic substances (HS) are the main component of DOM [23] varying from $0.03 \text{ mg} \cdot \text{L}^{-1}$ for groundwater to $40 \text{ mg} \cdot \text{L}^{-1}$ for lakes [24]. Thanks to HS polyfunctionality, they strongly effect on the adsorption of any ecotoxicant onto colloid particles [25]. Thus, the present study is devoted to the evaluation of the effect of HS on the sorption of CIP in real environmental trace concentrations by magnetite silica-based sorbent. For this purpose, magnetite NPs (M) modified with organosilanes (tetraethoxysilane, T and 3-aminopropyltriethoxysilane, A) were used as a model of natural colloidal particles and a sorbent. In our previous research on MTA toxicity towards infusoria *Paramecium caudatum* [26] we demonstrated that the combined presence of the MTA-NPs at a concentration of $1.5\text{--}2 \text{ mg} \cdot \text{L}^{-1}$ and HA at a concentration of $20\text{--}45 \text{ mg} \cdot \text{L}^{-1}$ has a multiplier effect and allows increasing the survival rate of ciliates $> 70\%$ compared to MTA and HA alone due to the enhanced removal of CIP.

From biomedical point of view, the produced nanosystems based on mesoporous silica including magnetic-based can be considered as a potential system to be applied in bacterial infection treatment [18], for the diagnosis and therapy of various diseases such as in tumor therapy [27] and as contrast agents for bioimaging [28, 29], nanocarrier [30] for drug delivery [31], including for targeted ciprofloxacin [31]. A simple and inexpensive dispersive solid phase extraction method was used by Nosratsehi et al. [32] based on $\text{SiO}_2 @ \text{MCM-41-Co}_3\text{O}_4$ yolk shell as a sorbent for the extraction of favipiravir (5-fluoro-2-oxo-1 H-pyrazine-3-carboxamide, first used to treat Covid 19 disease) from plasma samples. Porphyrinoids coated silica nanoparticles was tested as capacitive sensors for COVID-19 detection from the analysis of blood serum volatolome [33]; niclosamide encapsulated in mesoporous silica and geopolymer was proved to be a potential oral formulation for COVID-19 (Niclosamide encapsulated in mesoporous silica and geopolymer: A potential oral formulation for COVID-19). The presence of polyanionic polyelectrolyte (HS) can be considered as promising chemisensitizing agents in therapeutic alternatives for any biopreparations due to their detoxification, anti-, and pro-inflammatory or anticancer and antiviral ability [34, 35].

2 Materials and Methods

2.1 Synthesis of Magnetite NPs

The bare magnetite nanoparticles (MNPs) were prepared by the coprecipitation method described in Ref. [36]. Briefly, 7.56 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Joint Stock Company “Bromine”, Russia) and 2.78 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Joint Stock Company “Altayskiy Chimprom”, Russia) were dissolved in 70 mL of H_2O , then 40 mL of 25% solution of NH_4OH was added at 50 °C under argon flow and vigorous stirring at 1600 rpm during 20 min. The NPs prepared were washed three times with deionized water and twice with alcohol to remove the synthesis residues then dried at 70 °C under vacuum, yielding 2.9 g of the product.

2.2 Synthesis of Magnetite-Silica NPs (MTA)

The synthesis of silica-coated magnetite NPs was carried out by the well-known Stöber method [37]. The previously synthesized MNPs were used as a core to be coated with TA. MNPs weighing 5.8 g were suspended in 300 mL of DI water. To 25 mL of tetraethoxysilane (hereinafter referred to as T, 98% purity, Sigma-Aldrich), 225 mL of H_2O and 350 mL of $\text{C}_2\text{H}_5\text{OH}$ were added with constant stirring at 600 rpm, and finally, a suspension of MNPs was added to the resulting solution. The pH of the suspension MT was adjusted to 9 by 5 mL of 25% of NaOH and placed on a shaker (New Brunswick Environmental incubator shaker G24) for 1 h at 150 rpm and 60 °C. The MT precipitate was separated from the solution using an Nd magnet (0.3 T) and washed with 300 mL of H_2O to remove excess T, then twice with alcohol for drying. The 3-aminopropyltriethoxysilane (further A, 98% purity, Sigma-Aldrich) was used as a NH_2 -silica precursor. MT NPs weighing 3.2 g were dissolved in 150 mL of a DI water/ethanol solution (1:1 vol/vol), and then 6.2 mL of A was added to the solution in an argon atmosphere at 40 °C for 2 h according to Ref. [38]. Molar ratio of A to T was used as a 1:4. The precipitate was isolated with a magnet (Nd, 0.3 T) and thoroughly washed with water and alcohol before analysis or further use. Finally, the MTA sample was vacuum-dried at 70 °C during 2 h, yielding 6.9 g of the product.

2.3 Characterization of Samples

The structure of the surface layer of NPs may have profound effect on the toxicity of NPs as a surface is the first to be contacted with the cells [26]. Therefore, X-ray diffraction analysis (XRD) method was used to investigate the phase composition and estimate the average particle size of samples using a Philips X-pert diffractometer (Philips Analytical, Eindhoven, The Netherlands, $\text{Cr-K}\alpha$ radiation, $\lambda = 2.29106 \text{ \AA}$) as revealed in Ref. [39]. Average particle size was determined with the Scherrer Equation using the full width at half maximum (FWHM) of all reflections in the Origin 2019 Pro software.

The lattice parameters established for M and MTA NPs were below than that of magnetite Fe_3O_4 as 8.396–8.400 Å (ICDD-PDF 19-629) but above than that of maghemite $\gamma\text{-Fe}_2\text{O}_3$ as 8.33–8.34 Å (ICDD-PDF 39-1346). The formation of non-stoichiometric $\text{Fe}_{3-\delta}\text{O}_4$, where δ can range from 1 (stoichiometric magnetite) to 1/3 (fully oxidized) [40] due to partial oxidation of Fe^{2+} during synthesis conditions.

The morphology of the NPs was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Prior to SEM imaging, the samples were sputter coated with a thin film (approximately 10 nm) of a gold-palladium (Au-Pd) alloy using a Bal-Tec SCD500 coater. The morphology of the sputter-coated samples was examined using a Sigma 500 VP FE-SEM (Carl Zeiss, Oberkochen, Germany) with an accelerating voltage of 3 kV.

For TEM analysis, the NPs were dispersed in deionized water using an ultrasonic processor (Fisherbrand, USA) set at 75% amplitude to facilitate homogenization and prevent particle aggregation. A 10 μL aliquot of the suspension was applied to a 200-mesh carbon-coated copper grid (Ted Pella Inc., USA) pretreated with a glow discharge cleaning system (PELCO Inc., USA) to enhance sample adhesion. After one-minute incubation at room temperature, excess liquid was carefully removed with filter paper. The prepared grids were then mounted on a TEM stage for further analysis. High-resolution TEM images were obtained using a Tecnai G2-20 transmission electron microscope (FEI Company, Hillsboro, OR, USA) with an accelerating voltage of 120 kV. Particle size distribution was determined by analyzing at least 100 particles per image using ImageJ software (National Institutes of Health, USA).

Mechanism of modification was proved using the Fourier transform infrared spectroscopy (FTIR) analysis in the range of 4000–400 cm^{-1} on a FTIR spectrometer (FTIR IR-200, ThermoNicolet, USA). The samples were pressed into pellets $\varnothing = 13 \text{ mm}$ with spectrally pure KBr.

The specific surface area and characteristics of the porous structure of samples were determined using N_2 adsorption-desorption analysis (Quantochrome). To prepare the N_2 adsorption isotherms, the volume of gas-adsorbate (N_2) sorbed by the surface of the samples studied was measured when a stationary flow of a gas He-N_2 mixture of a given composition was passed through them (the volume fraction of N_2 varies from 0 to ≈ 1) at a temperature liquid N_2 (77 K) and desorbed by heating (up to approximately 100 °C). Similarly, for desorption isotherms, the volume of N_2 desorbed from the surface of the studied samples was measured with a decrease in its volume fraction in the gas mixture from ≈ 1 to 0. The specific surface area and characteristics of the porous structure were calculated based on the adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods. Prior the measurement, the test samples were degassed and vaporized, and “thermally trained” for

30 min by heating in a stationary N₂ flow in a vacuum at 150 °C.

Particle surface charge (zeta-potential) was analysed using electrophoretic light scattering on Brookhaven apparatus at a wavelength of 633 nm with a solid-state He-Ne laser at a scattering angle of 173° at 25 °C. For the analysis, each sample was diluted in water to 0.1 g·L⁻¹. Before the analysis the samples were ultrasonicated (ultrasonic bath, 100 W, 40 kHz) for 10 s of ultrasonication followed by 100 s of standstill. Samples were analysed in a disposable zeta cuvette (DTS 1070) at their original pH (as in synthesis, ranging from 5.4 to 7.5). The pH values were measured prior and after the study.

2.4 Equilibrium Sorption Studies

A sorption technique was used to quantify CIP sorption onto the NPs in the presence of humic preparation (HP, sodium salt of humic acids, Powerhumus, Humintech, Germany; 5 mmol·g⁻¹ of COOH and OH-groups, Mw = 8 kD). For the adsorption experiments, 1 and 2 g·L⁻¹ of NPs and/or 0.01 and 0.05 g·L⁻¹ of HP were weighed and placed into a 200 mL conical flask and filled with 100 mL of water with CIP concentration of 5 mg·L⁻¹. All flasks were rotated at 150 rpm in the dark on a rotary shaker for 24 h at 23 °C. After the reaction time of 24 h, the NPs and the supernatant were separated as described above. At the end of the equilibration period, the suspensions were centrifuged at 1000 rpm for 10 min and the supernatants were extracted by syringe and filtered through a hydrophilic membrane (0.45 µm) for CIP determination by UV-Vis spectroscopy. After filtration, the pH of the supernatant was measured (Supplementary Materials, Table S1). Equilibrium CIP concentrations were determined by transferring 2 mL aliquots to UV-Vis cuvette. Samples were analyzed on a Solar UV-Vis spectroscopic system equipped with a fluorescence detector.

To determine the concentration of CIP in the presence of HP the spectrophotometric measurements, the CIP solutions and HP were prepared in different concentrations in water. The CIP concentration in the solution varied from 1 to 20 mg·L⁻¹, the HP concentration was stepwise increased up to 50 mg·L⁻¹. In addition, the influence of the pH on the spectral characteristics was studied with pH altering from 5 to 8. When preparing solutions of CIP in the presence of HP, the pH values levelled off for all samples at about 7.0).

The absorption spectra were registered using a Solar PB2201 spectrophotometer (Solar, Belarus) at room temperature. The measurements were performed in the spectral range 200–600 nm with 1 nm interval using standard quartz cuvettes with an optical path length of 10, 5, or 2 mm depending on the absorbance of the studied samples. After measurements all absorbances were normalized to 1 cm pathlength.

3 Results

3.1 Characterization of Samples (XRD, IR, BET Analysis)

The XRD was used for the analysis of phase composition and primary particle size of the samples. The M and MTA samples are well crystallized materials according to intense and broadened diffraction reflections (Fig. 1) with Miller indices of (220, ~45°), (311, ~54°), (400, ~66°), (422, ~84°), (511, ~91°), and (440, ~101°). According to the quantitative analysis carried out by the Rietveld method, all diffraction patterns of the samples can be attributed to samples with a face-centered cubic (Fd3m) lattice and, ultimately, to partially oxidized magnetite. The functionalization of TA during the sol-gel synthesis leads to a decrease in the concentration of stiochiometric magnetite. So, for bare magnetite the crystal cell parameter is 8.383 Å, while for TA functionalized NPs that made 8.364 Å.

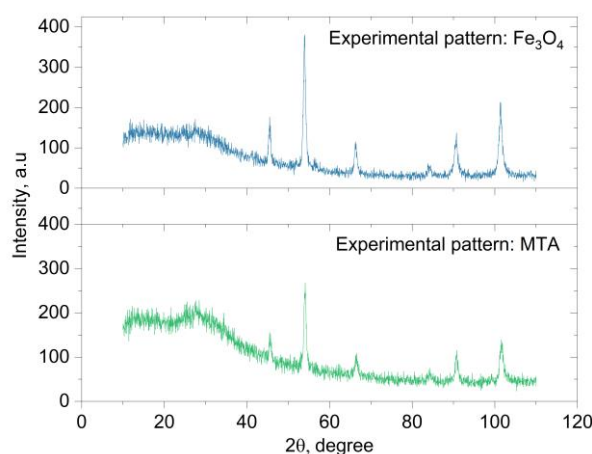


Fig. 1 XRD for M and MTA NPs samples.

The functionalization of TA leads to a slight change in the size of the coherent scattering region from 21.9 nm to 18.8 nm, which was calculated according to the XRD data using the Scherrer Equation. These values are in good agreement with the literature data [41, 42]. Moreover, according to transmission electron microscopy data, MNPs embedded in the TA matrix have an average size of 14 ± 3 nm and have a shape close to spherical (Supplementary materials, Fig. S6). This characteristic size and morphology indicates superparamagnetic nanoparticles behaviour. Scanning electron microscopy analysis of the MTA composite showed the presence of aggregated particles measuring 88 ± 15 nm with an ill-defined morphology (Supplementary materials, Fig. S6).

Analysis of the specific surface area (SSA) of the MTA NPs by the BET method and the average pore diameter by the BJH method found that the silica modification of M increase all surface characteristics for the MTA including the specific surface area, pore volume, and micropore volume (Table 1).

Table 1 Textural characteristics of samples.

Parameter	M	MTA
Pore volume, $\text{cm}^3 \cdot \text{g}^{-1}$	0.20 ± 0.01	0.96 ± 0.03
Pore width, nm	15.8 ± 0.9	32.7 ± 1.3
SSA MultiPoint BET, $\text{m}^2 \cdot \text{g}^{-1}$	63.8 ± 3.8	119.6 ± 5.4

The observed increase in the textural characteristics of magnetite-silica NPs is consistent with the results of studies [43].

Desorption hysteresis loops are observed on N_2 adsorption-desorption isotherms of the studied samples (Fig. 2). According to the BET classification in terms of adsorption isotherms shape (type IV) and to the International Union of Pure and Applied Chemistry (IUPAC) in terms of hysteresis loop shape (type H3), both samples have a mesoporous structure with a slit-like pore shape.

The mechanism of stabilization and functionalization of MNPs with TA was studied using FTIR spectroscopy. Si-OH silanol groups on the silica surface make it easy to organize the covalent attachment of ligands to the surface of M. To functionalize the TA surface, we used the sol-gel synthesis of NPs consisting of *in situ* hydrolysis and condensation of the sol-gel precursor (Fig. 3).

At the first stage of silica surface modification using TA, alkoxysilyl groups are hydrolysed with the formation of strongly grouped Si-OH. Groups of modifiers react with OH groups on the surface of silicon dioxide with the release of water and the formation of an anchor bond Si-O-Si-C. The introduction of A on the surface of MT NPs in our case is necessary to create terminal amino groups, which are subsequently connected in combination with commonly available classes of compounds in order to obtain functional and hybrid materials.

M is able to sorb SiO_2 due to the presence of OH-groups on the surface of iron oxide, which leads to the appearance of the Fe-O-Si bond and is confirmed by the appearance of transmission bands in the spectrum for MTA at wavelengths of 692 cm^{-1} , 583 cm^{-1} . The formation of the Si-O-Si bond characteristic of the silicon framework as a result of the sol-gel synthesis is confirmed by the appearance of a band at 1056 cm^{-1} , and the presence of C-H bonds indicates incomplete polymerization.

Comparison of IR spectra obtained with Fourier transform and Attenuated total reflection (ATR) spectra shows that ~12% of the Si-O-Si bonds are on the MTA surface. Comparison of the ATR IR and FTIR spectra shows that the free $-\text{NH}_2$ (790 cm^{-1} , 1633 cm^{-1} , 3424 cm^{-1}) or OH- groups (1633 cm^{-1} , 3424 cm^{-1}) localized partly on the NPs surface.

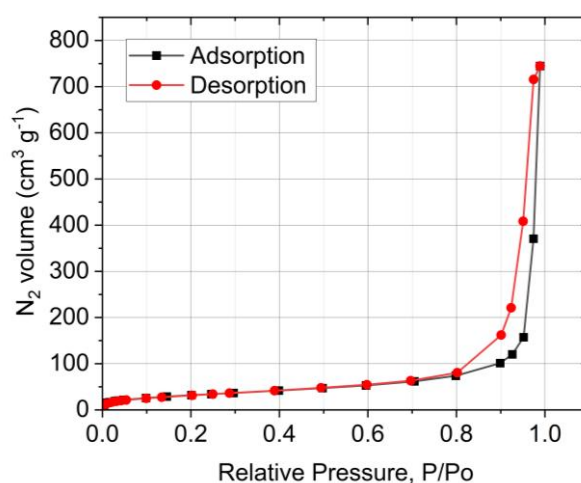


Fig. 2 Isotherms of N_2 adsorption and desorption of MTA.

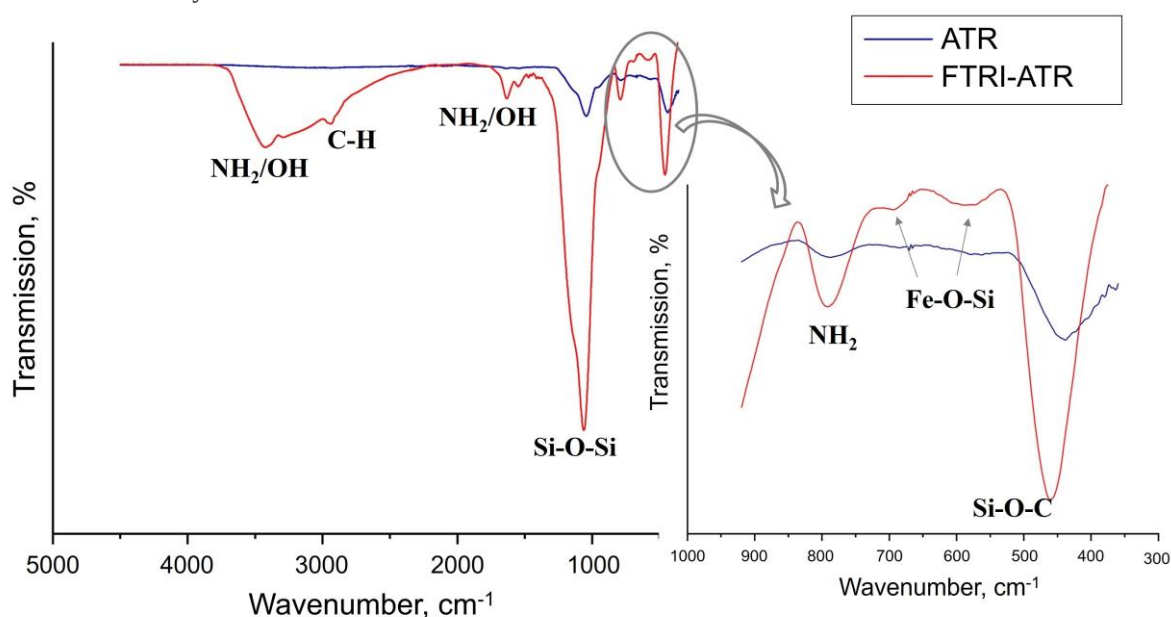


Fig. 3 IR-spectra of MTA: FTIR and ATR analysis.

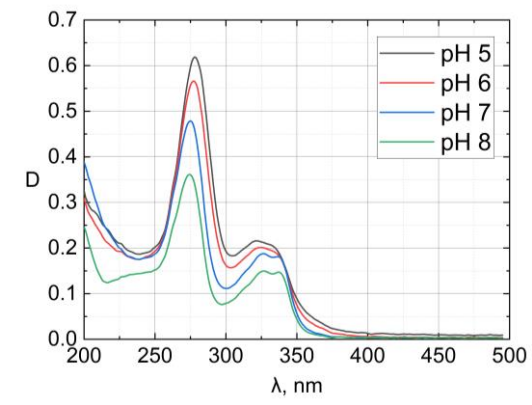


Fig. 4 UV-Vis spectra of a CIP solution in water at a fixed concentration $5\text{ mg}\cdot\text{L}^{-1}$ and different pH values.

3.2 Sorption Experiments: Spectrophotometric Measurements

Optical methods based on the measurement of absorption spectra make it possible to expressly analyse water pollutants by the absorption bands of the pollutant [44]. In the case of CIP, the UV absorption bands with maxima at 270–280 nm and 320–330 nm can be used. However, an obstacle in determining the concentration of CIP in natural or technological water is the presence of HS occurring in natural or waste water. The HS have high absorbance in the UV range and monotonically decreasing light absorption towards longer wavelengths, almost disappearing at about 500 nm [45, 46]. The proposed in this work method of CIP quantification in water in presence of HP was applied to determine the antibiotic concentration in an aqueous medium after its partial removal by various sorbents.

3.2.1 Absorption Spectra of CIP in Water at Different pH Values

When considering the CIP absorption spectra, one could notice the UV-band with a higher intensity at $\lambda_{\text{max}} = 270\text{--}280\text{ nm}$, and the second UV-band with a lower intensity at $\lambda_{\text{max}} = 320\text{--}330\text{ nm}$. Upon changing the pH of the medium at a constant CIP concentration, the following changes in the absorption band occurred: the

shift of maximum position and the change in absorbance value. The intensity of the UV-bands decreased with a change in pH from 5 to 8 (Fig. 4).

To avoid the problem with alteration of maximum position with pH we suggest to quantify absorption intensity not by the absorbance value D taken at certain wavelength, but by the area under the absorption curve (S) in the wavelength range from 260 to 300 nm. The calculation confirmed the dependence of the absorption intensity on the medium acidity: in solution with pH 5–6, the CIP absorbance turned out to be approximately 30% higher than in solutions with pH 7–8.

The dependence of the area S of the antibiotic absorption on the CIP concentration C was plotted (Fig. S1, see Supplementary Materials). This dependence turned out to be proportional, the coefficients of proportionality (k) are given in Table 2 for the studied pH values. The proportionality of the dependence allows it to be used to determine the CIP concentration in water at different pH values. The general formula for determining the concentration C will be as follows: $C = K \cdot S$, where $K = 1 \cdot k^{-1}$ is an empirical coefficient depending on the pH of the medium. The K values are shown in Table 2 for the studied pH values of the aqueous solution. Thus, it is possible to obtain a calibration dependence of the absorption band area of CIP on concentration to determine the antibiotic concentration in water with known pH.

Table 2 Values of coefficients k and K for different pH values of an aqueous solution.

pH	$k, \text{ nm}\cdot\text{L}\cdot\text{mg}^{-1}$	$K, \text{ mg}\cdot(\text{L}\cdot\text{nm})^{-1}$
5	3.40	0.29
6	3.37	0.30
7	2.53	0.40
8	2.25	0.44

3.2.2 Absorption Spectra of HP and Mixtures of CIP and HP in Water

The UV-Vis spectra of the HP solution in water is a monotonically decreasing curve, the intensity of which decreases in the direction of increasing wavelength (Fig. 5).

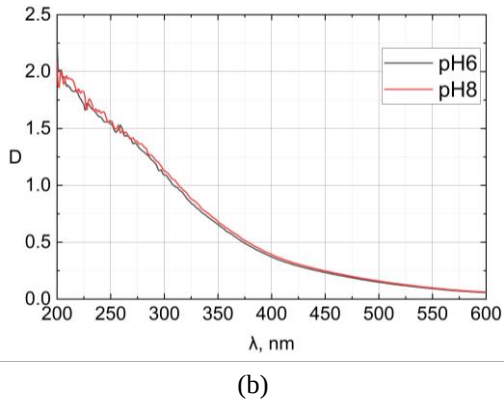
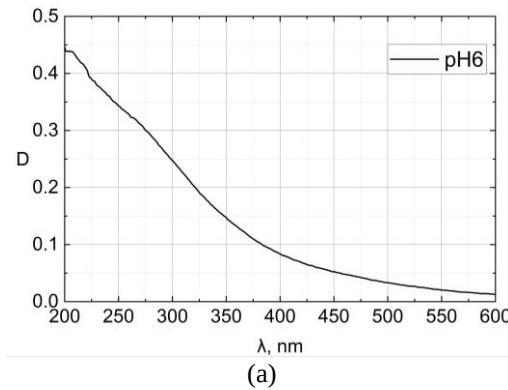


Fig. 5 (a) UV-Vis spectra of a HP ($10\text{ mg}\cdot\text{L}^{-1}$) at pH 6; (b) Absorption spectrum of a HP ($50\text{ mg}\cdot\text{L}^{-1}$) at different pH.

The absorbance value at each wavelength is almost independent on the pH of the medium. The absorption spectrum of the (CIP+HP) mixture is shown in Figs. S2 and S3 (Supplementary Materials).

HS are soluble in neutral and alkaline media [47]. This property varies depending on the chemical composition and origin of the HS. In an alkaline medium, phenolic and carboxyl groups are deprotonated (pK_i are approximately 4 and 9), negatively charged groups are repelled, and HP molecule acquires linear configuration. As the pH shifts to the acidic region, the functional groups of HS are protonated, the repulsive effects are minimized, and the molecules acquire a helical conformation, in which the hydrophobic regions are located in the inner part of the structure, and the hydrophilic parts are in contact with the aqueous medium. In this case, an increase in the concentration of HS can lead to the inaccessibility of reactive groups and steric hindrances in the CIP sorption. Fang et al. [48] noted that dissolved HP can act as an electron shuttle to accelerate electron transfer and CIP degradation.

The algorithm with the subtraction of the absorption band of the HP was repeated for all concentrations of the antibiotic in solution studied: 5, 10, 15, and 20 $\text{mg}\cdot\text{L}^{-1}$ (Fig. 6).

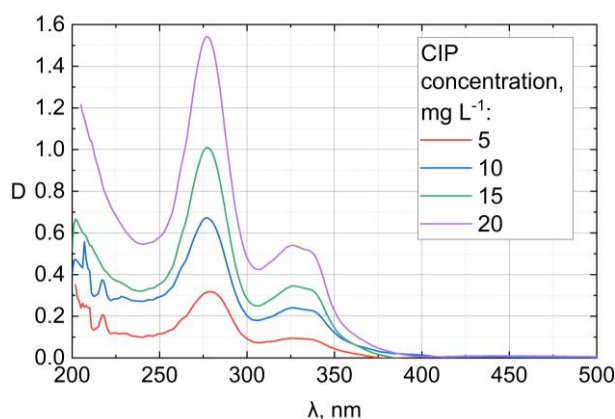


Fig. 6 UV-Vis spectra of CIP at different concentrations in water with the addition of HP at a concentration of 50 $\text{mg}\cdot\text{L}^{-1}$. Absorption of HP was subtracted from the spectrum of the (CIP + HP).

3.2.3 Calibration Curves for CIP

Determination in Water in Presence of HP

As a result, the dependence of the CIP absorption band area S on the CIP concentration obtained from the absorption spectrum of a multicomponent solution by subtracting the HP absorption band was plotted. This dependence also turned out to be proportional with slopes close to those obtained earlier for aqueous solutions of the CIP ($\text{pH}=8$) without HP (see Table 2). The similarity of the shape of the CIP absorption bands in the absence and with the addition of a HP (compare Figs. 6 and 7) led to the conclusion that there are no noticeable interactions between HP and antibiotic.

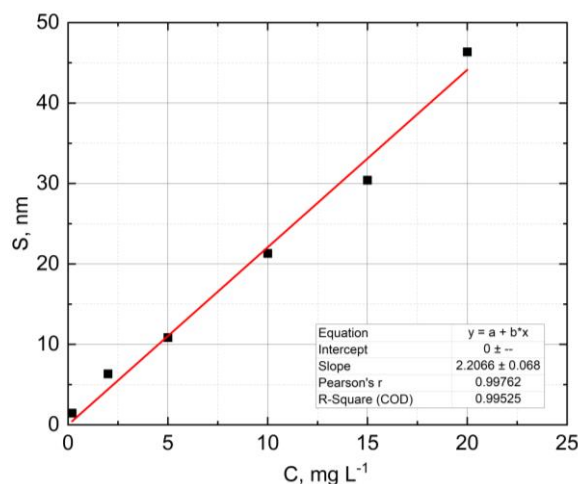


Fig. 7 Dependence of the area of the absorption band of CIP when the spectrum (HP) is subtracted from the spectrum (CIP+HP) on its concentration in the sample.

Thus, even in the presence of HP, the same formula can be used to determine the concentration of the antibiotic CIP in the aquatic environment: $C = K \cdot S$, where $K = 1 \cdot k^{-1}$ is an empirical coefficient determined as an average value according to Table 3.

Table 3 The coefficients k and K for the mixtures of HP and CIP.

Sample	k , $\text{nm}\cdot\text{L}\cdot\text{mg}^{-1}$	K , $\text{mg}\cdot(\text{L}\cdot\text{nm})^{-1}$
CIP (concentration 5, 10, 15, or 20 $\text{mg}\cdot\text{L}^{-1}$) + HP (50 $\text{mg}\cdot\text{L}^{-1}$)	2.21	0.45

3.2.4 Absorption Spectra of CIP in Water in the Presence of HP and MTA

The study of sorption properties of MTA in the presence of CIP showed that the addition of HP to a solution with pH 6 and 8 leads to pH equalization to ~ 7 . The introduction of the MTA NPs as a sorbent into a system with CIP incubated with HP leads to a 2-fold increase in the sorption capacity (Fig. 8).

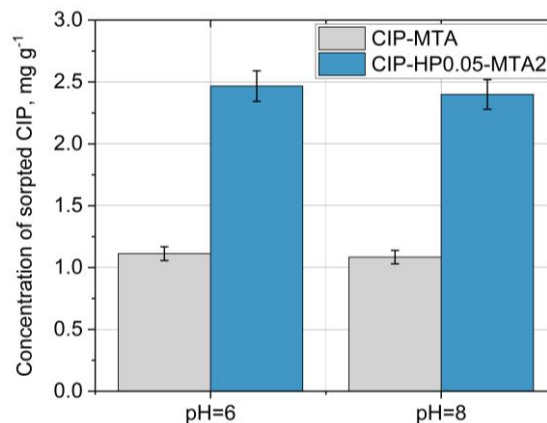


Fig. 8 Concentration of CIP sorted by MTA with and without of HP at different pH.

3.3 Proposed Mechanism of Sorption CIP by MTA and HP: Zeta Potential Measurements

To understand the mechanism of CIP sorption by NPs at various pH, the surface charge of NPs in terms of zeta potential was analysed using the dynamic and electrophoretic light scattering method. Dynamic light scattering is one of the most commonly used photonic methods for estimating the hydrodynamic radius, ζ -potential, polydispersity of nanoparticles, as well as for studying changes in these parameters upon interaction or aggregation of molecules and particles [49]. CIP is a zwitter-ionic compound. Below pH 5.9 ($pK_{a1}=5.9$), the predominant CIP species are cations. The surface of MTA is presented as positively charged, which causes an electrostatic repulsion between the available cationic species CIP and MTA.

The pH value is a key parameter that is critical for the removal of CIP molecules from aqueous systems because it affects adsorbate ionization, ion competition, and deprotonation of sorbent functional groups. The study of the dependence of the MTA zeta potential on pH showed (Fig. 9) that the isoelectric point of the NPs is at pH 5.5 (pH_{IEP}), which indicates the presence of a small amount of free amino groups on the surface. In the range $pH < 4$ and $pH > 6.5$, the zeta potential is greater than ± 25 mV, which indicates the stability of the sample due to electrostatic repulsive forces.

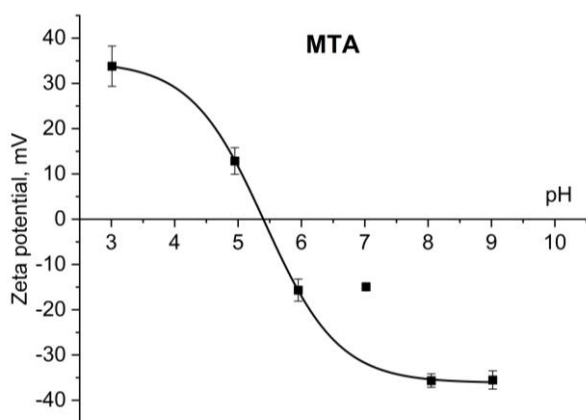


Fig. 9 The function of zeta potential of NPs of pH.

According to Refs. [50, 51], CIP carbonyl groups are deprotonated at 5.9 (pK_{a1}), and amino groups are deprotonated at 8.9 (pK_{a2}), which, for example, differs from the data of Wu et al. [52] reporting 6.1 and 8.7. After all, CIP can have different surface charges and exist as a cation, anion, and zwitterion [53], as shown in Fig. S5. With a total negative surface charge, absorption occurs through cation exchange with the protonated amino group. With a net positive surface charge, sorption occurs due to complex interactions of deprotonated carboxyl groups [54]. This is where the adsorbent IEP (pH_{IEP}) comes into play.

Below pH 5.9 ($pK_{a1} = 5.9$), the predominant CIP species are cations; under these conditions there is a high

concentration of the H^+ ions with smaller ionic radii and a higher adsorption capacity, which hinders the adsorption of CIP molecules creating competition between excess protons in solution and cationic CIP molecules (protonation of $-NH_2$ groups). Also, according to electrophoretic light scattering data, at $pH < pH_{IEP}$ (5.5), the MTA surface appears to be positively charged, which causes an electrostatic repulsion between the available cationic species CIP and MTA (Fig. 10).

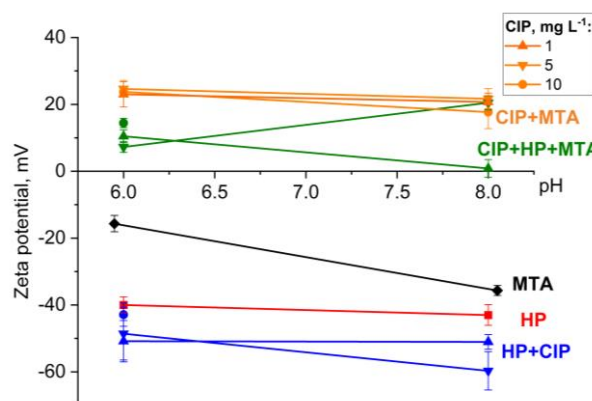


Fig. 10 Effect of HP and CIP adsorption on the surface charge of MTA NPs at different pH (0.05 $g \cdot L^{-1}$ of HP and 2 $g \cdot L^{-1}$ of MTA).

Thus, lower CIP sorption at lower pH values can be attributed to competitive sorption and saturation of adsorption sites on the MTA sorbent surface with hydrogen ions along with repulsive forces between CIP molecules and the protonated surface [55]. When the pH shifts to the alkaline region, the competition between protons and antibiotic molecules decreases and leads to an increase in the percentage of removal. If we talk about the mechanism, then an increase in pH leads to the interaction of CIP molecules with the functional groups of the sorbent (amino and hydroxyl groups) by ion-exchange mechanisms, which leads to an increase in the negative surface charge and electrostatic attraction, and, ultimately, to a higher efficiency of removal of CIP.

In addition, in the pH range ($pK_{a1} = 5.9-8.9$), CIP molecules are in an insoluble state and have a higher hydrophobicity, which leads to a hydrophobic interaction between the adsorbent/adsorbate and an increase in adsorption efficiency [55]. Moreover, at $pH > pK_{a2}$, a tendency to a decrease in the removal efficiency was recorded, which could be due to the electrostatic repulsive interaction between the negatively charged MTA surface (deprotonation of $-OH$ groups) and CIP molecules, as well as due to the saturation of MTA binding sites with CIP molecules. The recharging of the sorbent surface during the sorption of CIP from negative to positive may be associated with nonequivalent adsorption of the antibiotic on the NPs surface (an excess of antibiotic).

Thus, based on the electrostatic mechanism, it can be assumed that the higher sorption of CIP on the MTA

surface will be observed in the range of pH 5.9–8.9, where the negatively charged surface of the sorbent and the positively charged amino groups of CIP will be attracted. HA have a negative charge over the entire range of pH [56]. At the same time, the addition of CIP does not lead to a significant change in the zeta potential: the zeta potential value increases from -40 mV to -50 mV, probably due to sorption or the presence of CIP in solution, which can be adsorbed on the surface of HP due to positively charged amino acids groups.

At the same time, the addition of HP to the MTA-CIP complex leads to a decrease in the positive charge due to the dominance of negatively charged groups [57] on the HP surface compared to the CIP-MTA surface. The concentration of CIP does not lead to a change in the charge of MTA and HP.

4 Conclusions

The absorption properties of nanoparticles towards widely used antibiotic ciprofloxacin (CIP) in the presence of humic preparation (HP) as a model of dissolved organic matter (DOM) were analysed using spectrophotometric and electrokinetic studies. In absorption spectral measurements, the proportional dependence of the CIP absorbances and its concentration was established, and it was noticed that the absorption maximum shifts to a shorter wavelength range (278–274 nm) with pH increased from 5 to 8. Therefore, we suggested to use as a quantitative parameter of CIP concentration the area under the UV bands in the CIP absorption spectra. In presence of HP we subtracted the shapeless absorption spectrum of the HP to get CIP absorbances, which coincided with the previously obtained spectral absorbances for pure antibiotic. The fact that the absorption spectra of a multicomponent solution of CIP and a HP are a superposition of their individual absorption spectra indicates the absence of noticeable interactions occurring between the CIP and HP.

Analysis of the absorption spectra of CIP in the presence of silica-based magnetic NPs at different pH showed the influence of pH and HP in the CIP-MTA system. Thus, the sorption of CIP NPs increases by a factor of 1.5 when pH changes from 6 to 5. The introduction of NPs into a system with CIP incubated with HP leads to an increase in the sorption capacity by more than 2 times.

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Based on electrokinetic measurements, the mechanism of interaction in the CIP-HP-MTA system was proposed. Thus, in a three-component system, the surface is completely recharged from negative to positive: the MTA surface charge changes from -15 (pH 6) and -30 mV (pH 8) to $+10$ (pH 6) and $+2$ (pH 8), respectively. With an increase in pH from 6 to 8, CIP approaches the zwitterionic form, while the adsorption capacity of the formed MTA NPs increases, since the interaction of neutral CIP with the negatively charged surface of the obtained MTA NPs became more possible, but CIP is less soluble. At pH above 8.8, both CIP and the formed MTA NPs were negatively charged, which limited the interaction of CIP with the surface of the formed MTA NPs.

The study provides novel scientific information as NPs are increasingly produced and studied for various biomedical and environmental applications, including sorption of new emerging ecotoxins (pharmaceuticals), however the assessment of DOM contained in natural water even in trace concentrations should not be ignored. A systematic investigation will be a subject of future study of the adsorption performance towards CIP, by varying the initial pH, contact time and initial CIP concentration.

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Data Availability Statement

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

Disclosures

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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