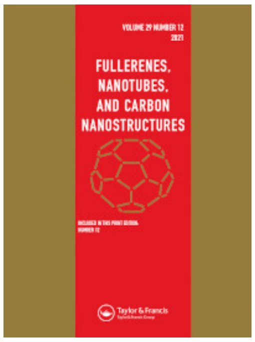

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The mechanisms of fluorescence quenching of carbon dots upon interaction with heavy metal cations

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ABSTRACT
The paper presents the results of a study of the interaction of heavy metal cations Fe^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Ag^{+} with carbon dots synthesized by the hydrothermal method in water. It was found that all the studied cations quench the fluorescence of nanoparticles to one degree or another. The series of cations were determined according to the degree of their influence on the fluorescence of carbon dots. The mechanisms of quenching the fluorescence of carbon dots upon interaction with cations have been investigated. It is shown that the quenching of the luminescence of nanoparticles in the presence of the investigated cations of heavy metals has a complex character. The observed changes in the intensity of fluorescence of carbon dots are the result of a superposition of several factors—electrostatic interactions of metal cations with surface fluorophores of carbon dots, aggregation of nanoparticles, and the effect of an inner filter for iron ions.

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KEYWORDS
Carbon dots; nanosensors; heavy metal ions

1. Introduction

At present, the problem of control of the content of various substances in multicomponent media is particularly acute: whether it is the simultaneous determination of the content of sugar and iron in human blood, monitoring the course of chemical reactions in various technological processes, monitoring the presence/absence of harmful impurities in tap water, etc. An increase in the concentration of heavy metals in wastewater as a result of many industrial processes[1] has an extremely negative effect on human health: it causes cardiovascular disorders, neuronal damage, renal injuries, and risk of cancer and diabetes.[2] To date, sensors based on various physical principles are widely used to determine the content of specific substances in media: optical sensors based on changes in absorption or luminescence properties as a result of the interaction of analytes with chromophores or sensor fluorophores, gravimetric piezoelectric quartz sensors based on the determination of changes in mechanical properties of the sensor for determining the amount of a substance, electrochemical, magnetic and others.[3] Actively investigated carbon dots (CDs) with intense and stable luminescence have broad prospects for their use as optical nanosensors in problems of diagnostics of multicomponent media.[3,4] Such prospects are provided due to CDs properties—the sensitivity of the fluorescence (FL) of CDs to changes in the characteristics of the environment—temperature, pH, the presence of various ions and molecules.[5–10]

There are various methods for the synthesis of CDs, while CDs synthesized by different methods have different physicochemical properties.[11–13] The hydrothermal synthesis method is relatively new and the main idea of the method is that the precursor(s) are exposed to high temperatures and pressures for several hours, followed by purification from reaction by-products. Depending on the selected precursors and reaction parameters (processing time and temperature conditions), CDs are obtained that differ significantly in their physicochemical properties.[14,15] This method makes it possible to synthesize CDs with previously known characteristics, in particular, with a known fluorescence response to the presence of various ions, that is, it makes it possible to create nanosensors based on carbon dots to solve narrowly targeted problems.

Known works,[16–24] which showed the successful use of CDs, obtained by the hydrothermal method, as sensors of various ions in liquid media. Thus, in Refs. [16–20, 23, 24], the possibility of using CDs as a nanosensor for determining the concentration of ferric ions was investigated. The use of carboxymethylcellulose and linear polyethyleneimine as precursors for the hydrothermal reaction in Ref. [16] made it possible to obtain a selective Fe^{3+} nanosensor with a good linear correlation of CD fluorescence intensity with iron ions concentration in the concentration range of 1–400 μM with a detection limit of 0.14 μM. In work [18], citric acid and polyvinyl pyrrolidone were used as precursors of the hydrothermal reaction. The authors studied the effect of cations Cu^{2+}, Mn^{2+}, Ca^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Na^{+}, Mg^{2+}, Ni^{2+}, Ag^{+}, Pb^{2+}, K^{+}, Co^{2+}, Cd^{2+}, and Hg^{2+} on the fluorescence of synthesized CDs. They found that the fluorescence intensity of CDs significantly decreased only in the presence of ferric (III) ions. This allowed the authors to create a

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nanosensor to detect Fe^{3+} ions within a range of ion concentration 0–300 μM with a detection limit of 45.5 nmol/L. The authors of publications[16,18] assumed that the response selectivity of CDs with Fe^{3+} among other metal ions was ascribed by the particular affinity of Fe^{3+} for the oxygen/nitrogen electron donors, which results in the coordinate covalent bond formation between these atoms. In work [20], in which it is also proposed to use CDs synthesized by the hydrothermal method from glucose and m-phenylenediamine as a luminescent sensor of ferric iron, the authors explain the observed results by the manifestation of the effect of an inner filter: iron cations, in contrast to other studied ions, have a wide absorption band in the region of 320 nm. It is radiation with this wavelength that was used to excite the FL of CDs.

In Refs. [21, 22] the use of CDs as sensors for the detection of lead ions in liquid media was demonstrated. In Ref. [21], the selectivity of FL quenching in the presence of lead ions was explained by the fact that Pb^{2+} had a stronger affinity and chelated fast with hydroxyl groups existing on the surface of CDs in comparison with other metal ions. In the work,[22] authors explained the quenching of the FL of CDs upon interaction with lead ions by connection of Pb ions to the CD in the forms of $=C\text{-}(COO)_2Pb$, $=C\text{-}COOPb^+$, $=N\text{-}Pb(OH)^+$, and $\equiv C{:}Pb^{2+}$ (Cπ-cation interactions). It should be noted that the above studies only consider the predominant quenching of CDs fluorescence due to one ion, while the effect of other ions present in the media on the CDs fluorescence is not investigated or taken into account.

Thus, in the literature, the use of CDs as nanosensors for heavy metal ions has been demonstrated more than once. Despite the successes in the development of optical nanosensors based on CDs, the existing sensors are "sharpened" for the definition of only one ion, that is, such sensors cannot be used to monitor many different heavy metal ions in a medium at once. At the same time, in most scientific and applied problems, it is required to simultaneously monitor a number of ions with high sensitivity in a multicomponent medium in real time. Obviously, for this it is necessary to know the mechanisms of interactions of CDs with ions present in the medium and to study the effect of these interactions on the FL of nanoparticles. This work is devoted to the study of the mechanisms of changes in the FL of carbon dots as a result of their interaction with several heavy metal ions in aqueous media.

2. Experimental

2.1. Materials

As objects of study, we used two samples of carbon dots—CD-V and CD-B (V—the fluorescence maximum is in the violet region of the spectrum, B—in the blue spectral region, see below), synthesized by the hydrothermal method using different precursors and reaction parameters. Trans-aconitic acid and aqueous ammonia solution (30%) were used as precursors for the preparation of CD-V, and citric acid and ethylenediamine were used to obtain CD-B. The synthesis of CD-V and CD-B is described in detail in the work.[25]

Table 1. Characteristics of CDs in an aqueous suspension with a nanoparticles concentration of 0.008 mg/mL.

CDs sample	Size, nm	Fraction, %	Zeta-potential, mV
CD-V	99 ± 14	66.5	−10.7 ± 0.5
	828 ± 76	33.5	
CD-B	30 ± 6	99.8	−39 ± 0.9
	398 ± 27	0.2	

To prepare aqueous solutions of heavy metal nitrates, we used the salts $AgNO_3$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$, $Cr(NO_3)_3$ (manufactured by SigmaAldrich) and deionized bidistilled water (Millipore Simplicity UV water purification system).

2.2. Methods

A Shimadzu RF-6000 spectrofluorimeter was used to obtain the fluorescence spectra of aqueous CDs suspensions in the presence and absence of the studied ions. Optical density spectra of aqueous solutions of the studied salts were obtained on a Shimadzu UV-1800 spectrophotometer. The IR absorption spectra of CDs evaporated from an aqueous suspension were obtained on a Varian 640-IR FTIR IR spectrometer equipped with a diamond crystal attachment operating on the principle of total internal reflection violation (ATR). Registration was carried out in the range 900–3800 cm^{-1}, the spectral resolution was 4 cm^{-1}. The sizes of nanoparticles in aqueous suspensions and the values of their zeta potentials were determined using a Malvern Zetasizer NanoZS.

3. Results and discussion

3.1. Characterization of CDs

As a part of the characterization of aqueous suspensions of CDs at the first stage, the values of zeta potentials and the sizes of particles in aqueous suspensions were determined. The data obtained are shown in Table 1.

It follows from the obtained results that the CD-V samples are more prone to aggregation in water as compared to the CD-B nanoparticles, which is explained by the lower values of the zeta potential of the suspension.

The composition of the surface functional groups of the synthesized CDs was determined using IR absorption spectroscopy. In Figure 1 shows the IR absorption spectra of CDs evaporated from an aqueous suspension.

As can be seen from Figure 1, on the surface of both types of CDs there are such functional groups as CH_2, CH_3 (1440–1480 cm^{-1}), C = O (1580–1630 cm^{-1}, 1650–1690 cm^{-1}), C-O (1210–1320 cm^{-1}), C = C (1620–1640 cm^{-1}), NH (1630–1660 cm^{-1}, 3380–3420 cm^{-1}, 3480–3540 cm^{-1}), O-H (3000–3600 cm^{-1}). From the analysis of the IR spectra of the samples, it can be seen that the composition of the surface of CD-B differs from CD-V by the presence of nitrogen-containing molecular groups C-N and C = N, which cause vibrational bands in the region of 1300–1320 cm^{-1} and 1460–1510 cm^{-1}, respectively. Thus, it can be concluded that the synthesized CD-V and CD-B are characterized by different sets of functional groups, that is, there is a heterogeneity of surface functional groups in nanoparticles of two types.

The FL spectra of the prepared aqueous suspensions of CDs with a concentration of 0.008 mg/mL were obtained on a spectrofluorimeter. The signal was excited by radiation with wavelengths from 250 to 450 nm with a step of 5 nm; the spectra were recorded in the spectral range from 250 to 750 nm with a step of 1 nm. The obtained excitation and FL spectra of CD-V and CD-B aqueous suspensions are shown in Figure 2.

As can be seen from the presented data, the FL spectrum of CD-V is a broad structureless band (Figure 2a), the maximum of which is located at 415 nm. According to the obtained FL excitation spectrum (Figure 2c), CD-V fluorescence is excited most intensely by radiation with a wavelength of 320 nm. It is this radiation that will be used in the future to excite the luminescence of CD-V aqueous suspensions.

The FL spectrum of CD-B also has no clear structure and is a broad band with a maximum at 442 nm (Figure 2d). According to the obtained FL excitation spectrum (Figure 2f), CD-B fluorescence is excited most intensely by radiation with a wavelength of 350 nm. It should be noted that the FL intensity of an aqueous CD-V suspension is approximately 5 times less than the FL intensity of an aqueous CD-B suspension with the same concentration of nanoparticles.

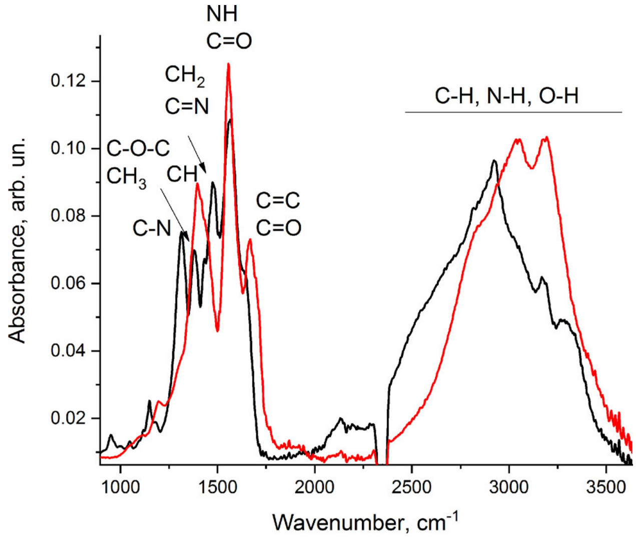

Figure 1. IR absorption spectra of CD-V (red curve) and CD-B (black curve).

3.2. Effect of heavy metal ions on the fluorescence of carbon dots in water

The following heavy metal cations were selected as objects of research of the effect of ions on the FL of CDs in an aqueous suspension: Fe^{3+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}.

Initial aqueous solutions of nitrates of the indicated ions with a concentration of 30 mM and aqueous suspensions of both types of CDs with a concentration of 0.008 mg/mL were prepared. To study the fluorescent properties of CD in the presence of heavy metal cations, we prepared aqueous mixtures-suspensions of CD with a fixed concentration of CD of 0.008 mg/mL and a variable concentration of ions. The concentration of each of the cations in the suspension mixture was varied in the range from 0 to 0.3 mM with a step of 0.03 mM. Taking into account the negative zeta potentials of both types of CD in suspensions and nitrate anions, the interaction of anions with the surface of nanoparticles could be neglected. The obtained FL spectra of CD in water and in all prepared suspension mixtures are shown in Figure 3.

As can be seen from the presented data, in the presence of all studied cations, the FL intensity of CDs decreases, that demonstrates the absence of shielding effect.[26] However, for different CDs and for different cations, this decrease manifests itself to varying degrees. Thus, the addition of zinc ions to an aqueous suspension of CD-V only slightly decreases the intensity of the FL CD, while the addition of ferric ions almost completely quenches the FL CD-V. A similar decrease in the FL intensity is observed for the CD-B sample, but to a lesser extent: the addition of iron ions to the suspension decreases the FL intensity of CD by ∼25%.

For all the obtained spectra, the relative change in the integral FL intensity of CDs in suspension mixtures and in water was calculated. The results of calculating such a relative change in the FL intensity of CD for several concentrations of cations are presented in Figure 4.

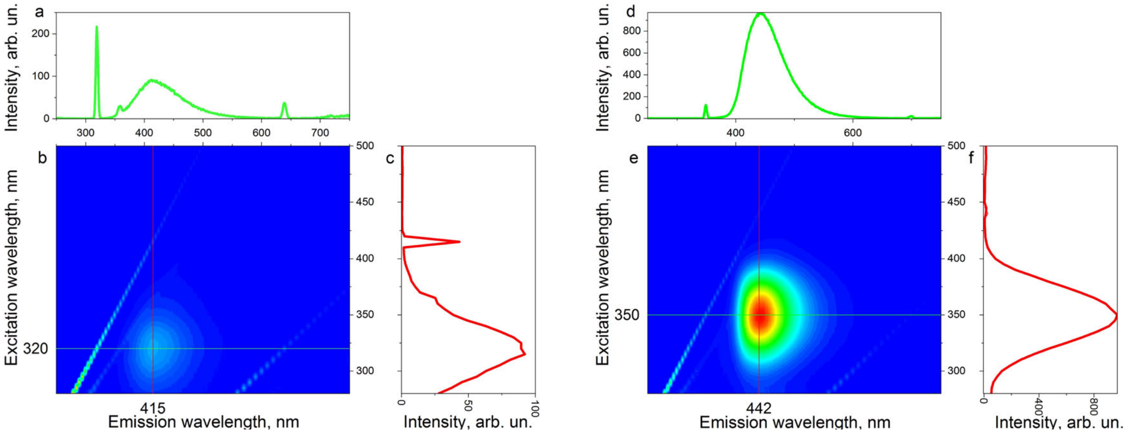

Figure 2. FL spectra of CDs (a) FL emission spectrum of CD-V upon excitation by radiation with a wavelength of 320 nm. (b) CD-V FL excitation-emission matrix. (c) FL excitation spectrum of CD-V when recorded at a wavelength of 415 nm. (d) FL emission spectrum of CD-B upon excitation by radiation with a wavelength of 350 nm. (e) CD-B FL excitation-emission matrix. (f) FL excitation spectrum of CD-B when recorded at a wavelength of 442 nm.

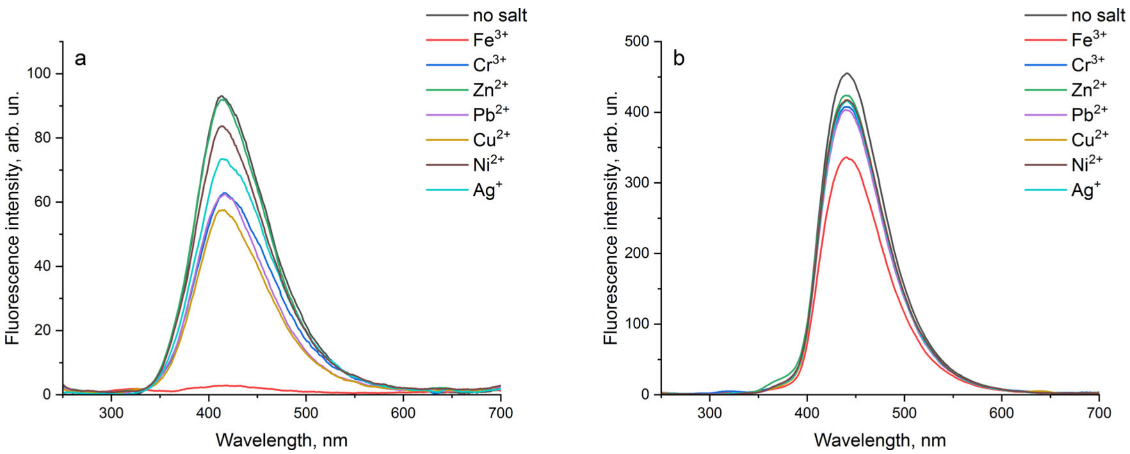

Figure 3. FL spectra of aqueous suspensions of CD-V (a) and CD-B (b) in the presence of the studied cations at the same concentration of cations (0.09 mM).

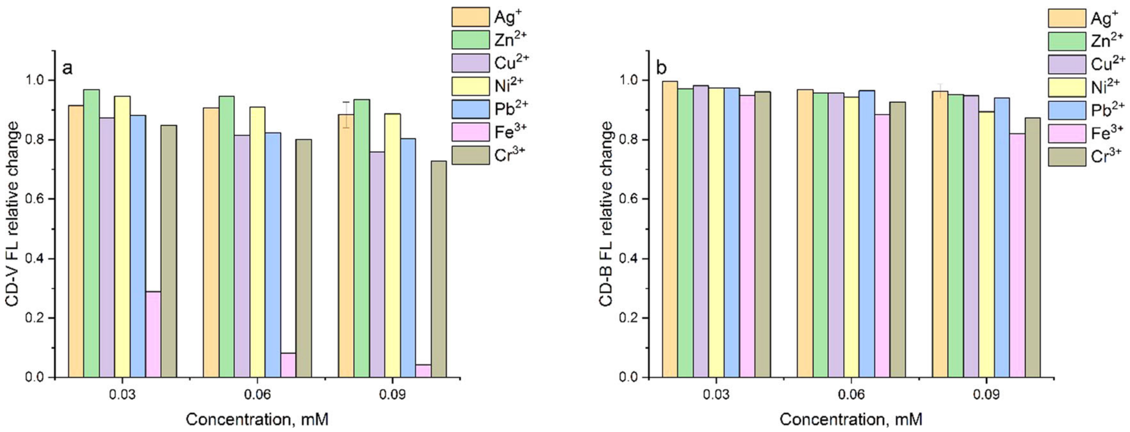

Figure 4. Change in the intensity of CDs FL in suspension mixtures in the presence of ions in comparison with CDs FL in the initial suspension. (a) CD-V, (b) CD-B.

Based on the obtained results, the series of cations were determined according to the degree of quenching of CDs FL by them:

$$\begin{aligned}&\text{for CD}-\text{V}: && Zn^{2+} < Ag^{+} < Ni^{2+} < Pb^{2+} \sim Cr^{3+} < Cu^{2+} \ll Fe^{3+}\\ &\text{for CD}-\text{B}: && Ag^{+} < Zn^{2+} \sim Cu^{2+} \sim Pb^{+} < Ni^{2+} < Cr^{3+} < Fe^{3+}\end{aligned}$$

The obtained series of the degree of influence of cations on the CDs FL do not completely coincide for the two types of CDs, which is explained by the difference in the composition of surface functional groups. However, there are general patterns: zinc and silver ions have the least effect on the FL intensity of CD of both types, while ferric ions quench the luminescence of both CD-V and CD-B the most.

3.3. Investigation of the mechanisms of quenching the fluorescence of carbon dots upon interaction with heavy metal cations

To be able to control the fluorescence properties of nanosensors, it is necessary to understand the mechanisms of formation and changes in the FL of CD as a result of interactions with the analyte. The results obtained in this work showed that all investigated cations quench CDs FL in aqueous suspensions. Therefore, studies were carried out on the mechanisms of quenching of CDs FL in water by various cations.

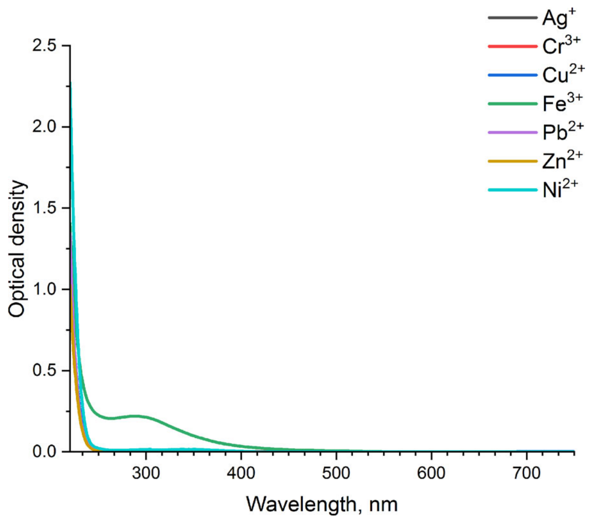

Figure 5. Dependence of the optical density of cation nitrates on the wavelength of the incident light.

3.3.1. Inner filter effect

In order to check the possible manifestation of the effect of the inner filter in mixtures-suspensions of CD and ions, the absorption spectra of solutions of all investigated inorganic salts were obtained (Figure 5). The spectra were recorded in the wavelength range from 200 to 750 nm.

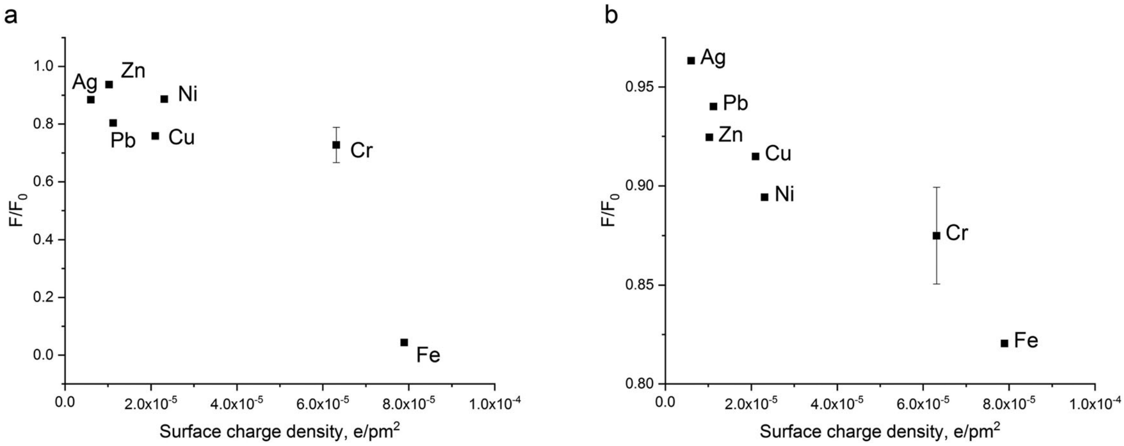

Figure 6. Dependences of the relative change in the FL intensity of aqueous suspensions of CD-V (a) and CD-B (b) in the presence of the studied cations on the density of the surface charge of the cation. "e" stands for elementary charge, pm—picometers.

As can be seen from Figure 5, in the range of radiation wavelengths from 250 to 400 nm, the optical density of an aqueous solution of Fe^{3+} nitrate is several times higher than the optical density of aqueous solutions of other salts. The values of the excitation wavelengths at which the FL intensity of CD-V and CD-B is maximum (320 nm and 350 nm, respectively) lie in the range where the optical density of iron is several times higher than the optical density of other cations; therefore, at the selected excitation wavelengths fluorescence of CD-V and CD-B is most strongly quenched in the presence of Fe^{3+} ions in suspensions (Figure 5). In the range of variation of the wavelengths of the incident radiation from 250 to 400 nm, the optical density of an aqueous solution of iron nitrate first increases with an increase in the wavelength of the exciting light, reaches a maximum value at $\sim$300 nm, and then decreases monotonically. The optical density of the iron solution at an incident radiation wavelength of 320 nm is almost twice that at a radiation wavelength of 350 nm; therefore, at the selected excitation wavelengths, the CD-V FL is quenched more strongly than the FL of CD-B.

Thus, one of the reasons for the greatest quenching of FL of both types of CD in the presence of iron (III) ions is the inner filter effect. In the presence of other ions in CD suspension mixtures, this effect is practically not manifested.

3.3.2. Electrostatic interactions

One of the reasons for quenching the fluorescence of CD in the presence of ions in water can be electrostatic interactions of the negatively charged surface of the CD with the studied cations. In this work, the dependences of the relative change in the FL intensity of aqueous suspensions of CD in the presence of cations on the density of the surface charge of the cation were calculated and plotted (Figure 6). The charge density of every studied cation was calculated as a ratio of ion charge to ion surface area. The relative change in the FL intensity was characterized by the parameter F/F_0, where F is the intensity of CD fluorescence in the presence of salt, F_0 is the intensity of CD fluorescence in the absence of salt.

It follows from the obtained results that the greater the surface charge of the cation, the more the fluorescence of the CD is quenched. That is, the more strongly the cation is attracted to the negative surface group of CD, the stronger the decrease in the FL intensity of CD. We explain the difference in the degree of FL quenching for different CDs by the difference in surface fluorophores in CD-V and CD-B, which clearly follows from the analysis of the FL excitation and emission spectra (Figure 2). Apparently, different surface fluorophores CD-V and CD-B react differently to the presence of cations. However, for each of the studied CD, the dependence of the relative change in the FL intensity of the CD on the density of the surface charge of the cation is clearly visible. The iron cation is clearly distinguished from the general trend in Figure 6(a), which is due to the significant contribution of the inner filter effect to the quenching of CD fluorescence.

3.3.3. Influence of the aggregation of carbon dots in the presence of heavy metal ions on the fluorescence of nanoparticles

Quenching of the fluorescence of CDs in suspensions may be due to the aggregation of nanoparticles. To test this mechanism for quenching of CDs FL, we measured the hydrodynamic diameters of nanoparticles in aqueous suspensions before and after the addition of cations. The results are shown in Figure 7.

As can be seen from the obtained data, the addition of cations to aqueous suspensions of CDs leads to the formation of aggregates of nanoparticles. Thus, an almost tenfold increase in the hydrodynamic size is observed when a solution of lead nitrate is added to an aqueous suspension of CD-V, and an almost twenty-fold increase in the size of nanoparticles when a solution of copper nitrate is added to an aqueous suspension of CD-B. However, from a comparison of the results obtained on the aggregation of nanoparticles and the change in the fluorescence of CD in the presence of metal cations (Figure 4), it can be concluded that the aggregation of particles does not have a decisive contribution to the change in the FL of CD, but is only one of the mechanisms of quenching the luminescence of CD.

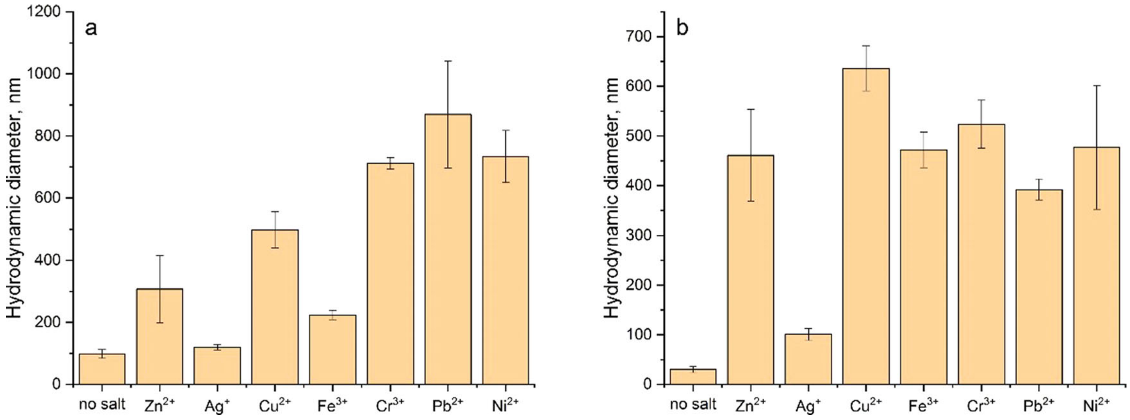

Figure 7. Values of hydrodynamic diameters of (a) CD-V and (b) CD-B aggregates in the presence of the studied cations. Concentrations of CDs and cations are constant and equal to 0.008 mg/mL and 0.3 mM, respectively.

Thus, the sizes of CD-V aggregates in the presence of zinc ions and in the presence of iron ions practically coincide within the experimental error, but the FL intensities of suspension mixtures differ by about 10 times. Similarly for CD-B: at practically the same size of aggregates of nanoparticles in the presence of zinc and iron cations, there is a significant difference in the FL of CD-B.

4. Conclusions

In this work, the interaction of heavy metal cations Fe^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Ag^{+} with CDs of two types CD-V and CD-B in water has been studied. It was found that all the studied cations quench the FL of nanoparticles to some extent. The series of cations were determined according to the degree of their influence on the fluorescence of CDs.

The mechanisms of FL quenching of CD upon interaction with cations have been investigated. It is shown that the quenching of the fluorescence of CD in the presence of the investigated cations of heavy metals has a complex character—the observed changes in the fluorescence intensity of CD are the result of the superposition of several factors.

It was found that one of the reasons for the greatest quenching of PL of both types of CD in the presence of iron (III) ions is the effect of the inner filter. In the presence of other cations in CD suspension mixtures, this effect is practically not manifested.

It follows from the results obtained that the greater the surface charge of the cation, the more the fluorescence of the CD is quenched.

Based on the analysis of the obtained sizes of CDs aggregates in aqueous suspensions in the absence and in the presence of cations, it was found that the aggregation of nanoparticles does not have a major contribution to the change of the FL of CDs, but is only one of the mechanisms for quenching the luminescence of CD.

The results obtained provide CD, synthesized by the hydrothermal method, broad prospects for use as a nanosensor for identification and determination of the concentration of heavy metal cations in liquid media.

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Disclosure statement

The given paper disclosures no conflict of interests.

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