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Aerogels based on reduced graphite oxide and cobalt oxide nanoparticles ($rGO@Co_3O_4$) as sorbents of antibiotics and dyes from aqueous solutions

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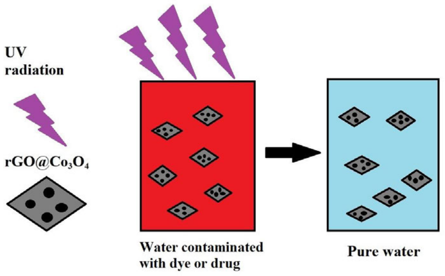
The effectiveness of an aerogel based on $rGO@Co_3O_4$ for purifying aqueous solutions from organic contaminants has been demonstrated. Experiments were carried out on the sorption of organic dyes (methylene blue, methyl orange) from solutions of varying acidity. The effective destruction of anticancer antibiotics (doxorubicin, mitomycin C) under the influence of UV irradiation in the presence of $rGO@Co_3O_4$ aerogel has also been shown.



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Currently, many processing industries, including paper, textiles, paints, plastics and leather, use organic pigments to color their products, the excess of which ends up in wastewater. Their presence in the aquatic environment prevents the penetration of sunlight, thereby reducing the photosynthesis of aquatic plants. Some dyes and pigments contain aromatic rings in their structure, which makes them toxic, non-biodegradable, carcinogenic and leads to cancer, mutagenesis and other serious problems in humans and animals. Therefore, the problem of removing dyes from aqueous solutions and their biodegradation is very relevant.[1–4]

Methylene blue (MB) and methyl orange (MO) were chosen as model dyes in this work. MB is an organic cationic dye belonging to the thiazine group and containing a phenothiazine ring. MO is an acid–base indicator, an organic anionic dye from the group of azo dyes. Both dyes are widely used for dyeing cotton, wool and silk, in medicine, in analytical chemistry and in microscopy, which contributes to intense wastewater pollution.

The cytostatic antitumor drugs mitomycin C (MMC) and doxorubicin (DOX), used in oncology, were chosen as model antibiotics in this work. The peculiarity of the use of these drugs in oncourology is that the patient is instilled with solutions of antitumor drugs, which requires a large amount of solutions and the removal of drugs after the procedures. MMC is an antitumor agent from the group of mitosan antibiotics. In the solid state, the antibiotic is isolated in the form of blue-violet crystals.[5] DOX is an anthracycline drug that interacts with DNA and inhibits the synthesis of nucleic acids.[6]

Graphene, graphite oxide and reduced graphite oxide (rGO) are widely used as sorbents for environmental remediation because they have significant specific surface area and adsorption capacity. However, graphite oxide and its reduced form are more easily dispersed in aqueous solutions due to the presence of hydroxide (–OH), carboxyl (–COOH) and epoxy (–C–O–C–) functional groups, making the processing, synthesis and application of these materials more convenient.[7] The carbon-containing layers in rGO are bonded to each other by van der Waals forces, resulting in the formation of delocalized π orbitals that can be used to form bonds with adsorbed aromatic compounds, which include most antibiotics and dyes.[4]

To increase the mechanical strength of rGO-based composites and the subsequent photodegradation of adsorbed dyes and drugs, it is advisable to introduce transition metal oxide nanoparticles into the carbon-containing material, which can change the concentration of charge carriers upon irradiation and transfer electrons to molecules of sorbed substances. Such properties, for example, are exhibited by cobalt oxide Co_3O_4, which is a magnetic semiconductor with a cubic spinel crystal structure and has catalytic and electrocatalytic activity.[3]

In this work, the sorption of the cationic dye MB and the aniline dye MO in media with different pH values and at different temperatures was studied.

Our previous studies have shown that the surface of rGO aerogel contains negatively charged oxygen-containing functional groups that can interact strongly with the protonated amine groups of the MB dye and, to a lesser extent, with the anionic MO dye. The adsorption process is also contributed by π–π interactions between localized π electrons in conjugated aromatic rings in rGO as well as in MB and MO molecules.[8–10]

Unlike MMC, the sorption of which by materials based on rGO has been little studied,[11] the interaction of composites containing cobalt oxide and rGO has been studied to a greater extent, which is explained by the longer use of DOX in the treatment of oncological diseases.[6]

It should be noted that systematic studies of the adsorption properties of rGO@Co_3O_4 aerogels in relation to cationic and anionic dyes and antitumor antibiotics depending on the pH and temperature of the environment have not been carried out. Therefore, the purpose of this work is to solve the urgent problem of creating rGO@Co_3O_4 composite aerogels based on rGO and cobalt oxide nanoparticles and using them as materials capable of sorbing antibiotics and dyes from aqueous solutions and causing their subsequent photodegradation under the influence of an external irradiation source. The rGO@Co_3O_4 aerogel was synthesized and characterized as described below.[†]

Figure 1(*a*) presents the results of X-ray phase analysis of powder aerogel based on graphite oxide and cobalt oxide. The diffraction pattern of the resulting rGO@Co_3O_4 composite clearly shows narrow peaks at 2θ angles of 18.96, 31.26, 36.86, 38.54, 44.8, 55.66, 59.36 and 65.26°, corresponding to cobalt oxide Co_3O_4 (JCPDS card no. 76-1802). The peaks corresponding to rGO are poorly identified due to the high content and better crystallinity of the Co_3O_4 phase.

The SEM results presented in Figure 1(*b*) indicate a layered structure of the rGO@Co_3O_4 aerogel; the inclusion of cobalt oxide particles is confirmed by elemental analysis data. The element content (%) of rGO@Co_3O_4 (C 17.61, O 60.33, Co 21.52, Mn 0.25, Cl 0.16, Ca 0.09) was determined by energy dispersive X-ray microanalysis.

The linear dependence of the specific magnetization on the magnetic field strength of the rGO@Co_3O_4 aerogel indicates the paramagnetism of Co_3O_4. At room temperature it is a normal spinel, in which Co^{3+} ions occupy octahedral positions.

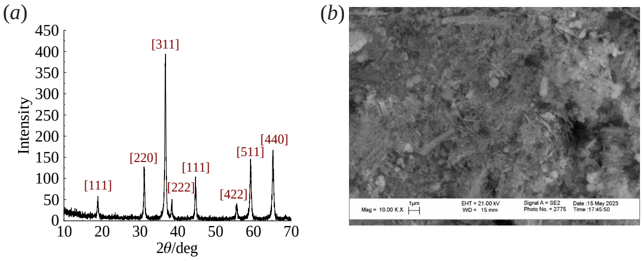

Figure 1 (*a*) XRD pattern and (*b*) SEM image of the rGO@Co_3O_4 composite.

The technique of sorption experiments has been described in detail previously.[12] In this work, we assessed the effectiveness of the sorption properties of the composite with respect to anticancer antibiotics and dyes.

To study the dependence of sorption efficiency on the MB solution medium, experiments were carried out in acidic (pH 3), alkaline (pH 10) and neutral (pH 7) environments. The pH of the solution was adjusted to the required value using solutions of hydrochloric acid and potassium hydroxide. From the experimental data it follows that the sorption efficiency is highest in a neutral environment and reaches a value of 58.5%, while in an acidic and alkaline environment the adsorption is significantly lower, 12.8 and 9%, respectively [Figure 2(*a*)]. According to the acid–base equilibrium isotherm, there are two equilibria for MB and rGO:

$$MB^+ + Cl^- + H^+ + \bar{e} \rightleftarrows MBH^+ + Cl^- \qquad (1)$$

and

$$rGO–H \rightleftarrows rGO^- + H^+. \qquad (2)$$

At low pH values, the hydrogen ion competes with the MB^+ cation and the MBH^+ form predominates. This means that the nitrogen contained in MB is protonated. In addition, a significant part of the rGO regions exists in the form of rGO–H, and the presence of such protonated forms reduces the sorption of MB. At higher pH values, the equilibrium shifts toward the formation of more rGO, which could increase the electrostatic attraction and the extent of MB adsorption, but this does not occur. Perhaps this contradiction is due to the deprotonation of carboxyl groups on the surface of rGO, as a result of which they lose the ability to interact with the N atoms of the amino groups of the dye.

From the experimental data for MO it follows that the sorption efficiency increases with decreasing solution pH, showing values of 65.71, 42.33 and 15.47% in acidic, neutral and alkaline environments, respectively. When carrying out sorption experiments with the anionic MO dye in an acidic environment, significant protonation of the nitrogen-containing groups of MO occurs. This leads to the appearance of a positive charge on the dye particles and increased electrostatic interaction with the surface of the rGO@Co_3O_4 composite. Note that the efficiency of MO sorption by rGO@Co_3O_4 aerogel in an acidic environment is significantly higher than that of the cationic MB dye due to greater protonation of MO molecules in an acidic environment.

To study the effect of the presence of Co_3O_4 nanoparticles on the sorption efficiency of MMC and DOX, two series of experiments were carried out. Due to the fact that some of the active sorption sites on rGO sheets are covered with cobalt oxide particles, rGO sorbs MMC and DOX more efficiently in the absence of Co_3O_4 [Figure 3(*a*)]. But during the experiments, it was noticed that the rGO@Co_3O_4 composite can be easily separated from the solution due to the mechanical strength of the aerogel, while the layers of pure rGO delaminate and it is impossible to isolate them after the experiment.

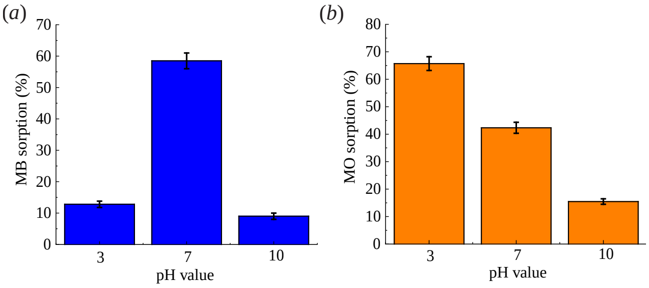

Figure 2 Dependence of sorption of (*a*) MB and (*b*) MO by the rGO@Co_3O_4 composite on the pH of the solution.

[†] *Synthesis of rGO@Co_3O_4 composite aerogel.* The initial graphite oxide was prepared by the improved Hummers method.[13] To obtain a composite aerogel, $Co(NO_3)_2·6H_2O$ (0.436 g) was dissolved in distilled water (8 ml), a suspension of graphite oxide (0.12 g) in distilled water (100 ml) was added, ultrasonic treatment was carried out for 30 min, and then concentrated ammonia solution (4 ml) was added. The resulting mixture was subjected to hydrothermal treatment in a closed autoclave at a temperature of 140 °C for 12 h. Then the mixture was filtered to separate the precipitate, which was thoroughly washed with distilled water and alcohol to remove impurities. The resulting solid was cryogenically dried on a Labconco apparatus at temperatures from −10 to 25 °C and a pressure of 0.5–0.7 mbar. The finished product was fired in a kiln at 400 °C for 6 h.

Characterization methods. X-ray diffraction (XRD) studies were carried out on a Rigaku D/MAX 2500 diffractometer (Japan) with Bragg–Brentano geometry and a rotating anode (CuKα radiation). Registration was carried out in a step-by-step mode in the 2θ range of 5–80° with a step of 0.02° and an exposure of 2 s per point. The obtained data were processed using standard packages of the WinXpow program.

Scanning electron microscopy (SEM) images were obtained using a Leo Supra 50 VP scanning electron microscope.

Magnetic properties were studied using a Faraday balance-type device (manufactured by ISSC UB RAS) in magnetic fields with a maximum strength of 18 kOe at room temperature. Data collection and processing were carried out using the Magnetometria software package.

UV-VIS absorption spectra were obtained on Perkin Elmer Lambda 950 and Perkin Elmer Lambda 35 spectrometers in the wavelength range 200–800 nm.

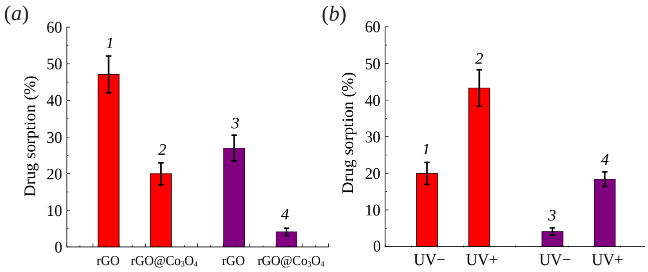

Figure 3 Efficiency of sorption of (*1*),(*2*) DOX and (*3*),(*4*) MMC by the rGO@Co_3O_4 aerogel from physiological solution: (*a*) effect of the presence of Co_3O_4 and (*b*) effect of UV irradiation of the solution.

To study the dependence of the efficiency of photodegradation of MMC and DOX under the action of UV radiation, two series of experiments were carried out with and without UV radiation at a wavelength of 254 nm.

Under the influence of UV radiation, electrons of mixed cobalt oxide are excited and transit from the valence band to the conduction band. The resulting electron–hole pairs enter into a redox reaction with antibiotic molecules located near the surface of the composite and cause their destruction, which is confirmed by a decrease in the signal in the UV absorption spectra of drug solutions. As a result, the solution cleaning efficiency increases from 5 to 19.5% for MMC and from 20 to 43.5% for DOX.

It is also possible to observe, both with and without irradiation, a higher efficiency of purification of solutions from DOX than from MMC. This is due to the fact that there are no aromatic fragments in the MMC molecule and, therefore, there is no π–π stacking.

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