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Disodium 1-(2-Pyridylazo)-2-oxynaphthalene-3,6-disulfonate: An Immobilized Reagent for Iron(III) Determination

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Abstract—The sorption properties of the fibrous sorbents of new types modified with hydroxylamine, ethylene diamine or hexamethylene diamine were studied. The possibility of their use for the disodium 1-(2-pyridylazo)-2-oxynaphthalin-3,6-disulfonate immobilization was shown and the optimal conditions for the determination of iron(III) in water were found.

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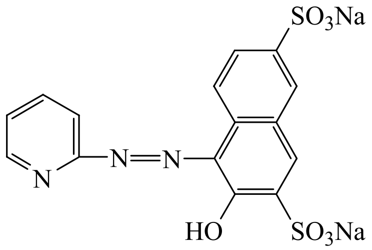
Currently, chelating sorbents obtained by the immobilization of organic reagents and characterized by the high efficiency and the ease of use are of great interest [1–3].

In this report the results of immobilization of some organic reagents on the polymeric fibrous materials are described. Owing to the use of the fibrous ion-exchange sorbents it is easy to combine the selective concentration of an element to be determined with a selectivity of its determination, while reducing the detection limit and increasing the analysis selectivity and rapidity [4–6].

Previous reports contain the results of the study of the mechanism of different reagents immobilization and features of the complexation on the solid polymer materials [7–9].

In this study we demonstrated the efficiency of the fibrous materials based on a polyacrylonitrile (PAN) modified with hydroxylamine in organic and aqueous media, as well as with hexamethylene diamine and ethylene diamine. The modified sorbents are insoluble in the solvents in which PAN is soluble indicating that the modifier molecules have actually reacted [10]. The carriers we used have good mechanical and chemical stability, high capacity, and unique kinetic properties, they can reduce the detection threshold significantly by increasing the resource of the sample solution at the insufficient sensitivity of color reaction.

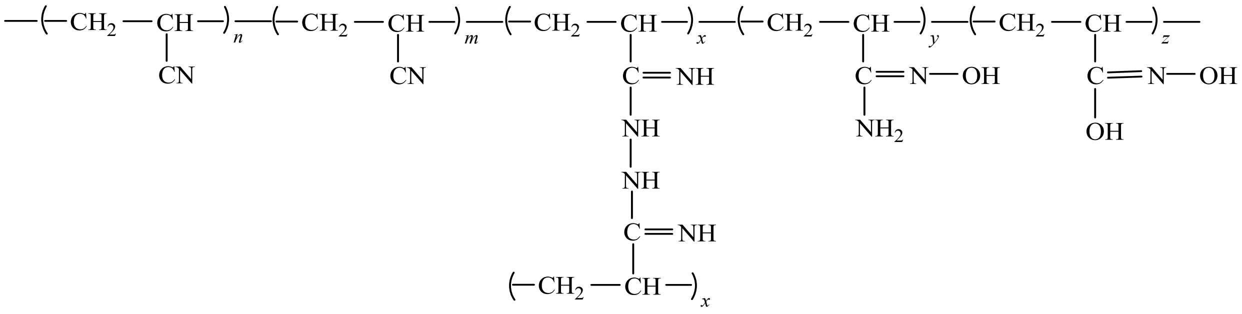
For the immobilization we used a reagent of pyridine series, the disodium 1-(2-pyridylazo)-2-oxynaphthalene-3,6-disulfonate.



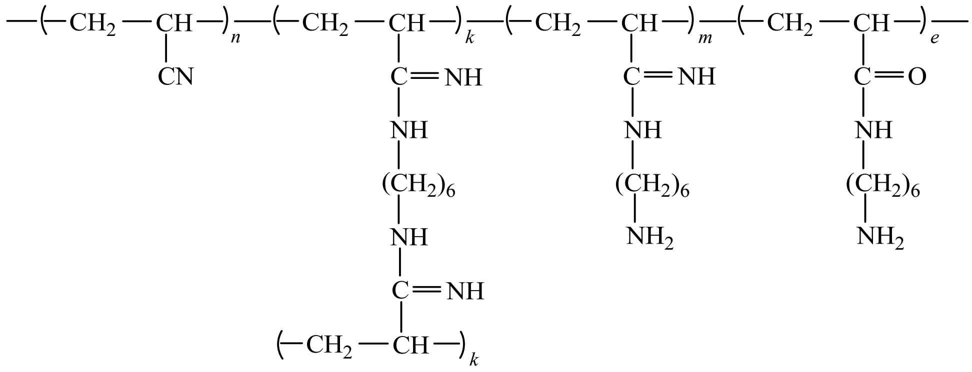
The disodium 1-(2-pyridylazo)-2-oxynaphthalene-3,6-disulfonate is a dark-red water-soluble powder, stable at the storage for a long time and characterized by a high sensitivity. The polymeric anion-exchange fibers were obtained by chemical modification of the industrial acrylic fiber Nitron with nitrogen-containing bases hydroxylamine (SMA-2), hexamethylene diamine (SMA-1), and ethylene diamine (SMA-3). These sorbents are non-woven beige fiber, resistant to acids and bases. Kinetics of chemical modification in aqueous solutions was studied in the temperature range from 60 to 100°C at various concentrations of hydroxylamine and hexamethylene diamine. On the basis of the results obtained the suitable conditions for the fabrication of the ion-exchange fibers with a static exchange capacity of 5.0–5.5 mg-eq/g (on 0.1 N HCl) were established.

Based on the IR spectroscopic and the potentiometric studies the following chemical structure was proposed for the polymer fibers obtained at the treating with hydroxylamine.

The treatment of Nitron with hexamethylene diamine affords the fiber containing both weakly and



strongly basic functional groups. In these cases diamines act also as cross-linking agent and modifier of nitrile groups simultaneously. Based on the results of the potentiometric titration and the IR spectral data, the fragment of SMA-1 molecules can be represented as follows:



The IR spectroscopic study of the initial fibrous carriers, organic reagents, and immobilized reagents showed that some absorption bands in the range of 3000–3600 cm^{-1} characteristic of the bending vibration of hydroxy and carboxy groups, and in the range of 1200–1100 cm^{-1} (SO_3H) are shifted.

Comparison of the spectra of the immobilized reagent and the starting organic reagent showed similarity of their functional-analytical groups responsible for complexation indicating retention of the reagent structure in the immobilized state (Table 1). The IR spectrum of the complex contains an absorption band at 598 cm^{-1} assigned to the stretching vibrations of the O–Fe bond [11], which is absent in the IR spectrum of the initial reagent

The fibrous anion-exchange polymeric materials based on the polyacrylonitrile immobilized with reagents form colored complexes in the polymer phase at the contact with an iron solution. To study the complexation of iron(III) with disodium 1-(2-pyridylazo)-2-oxynaphthalene-3,6-disulfonate we used diffuse reflectance spectroscopy. This method allows quantifying the content of the iron ions in the sample by the value of diffuse reflectance (*R*). The *R* value at the chosen wavelength was recalculated into the Kubelka–Munk function *F* by the formula: $F = (1 - R)^2/2R$ [12].

Table 1. Parameters of the IR spectra of the reagents and complex (cm^{-1})

Compound	$\nu(-SO_3H)$	$\nu_{N=N}$	ν_{OH}	ν_{CN}	ν_{O-Fe}
Reagent	1200	1628	3450	2244	–
Immobilized reagent	1172	1629	3450	2244	–
Complex	1171	1600	3441	2204	598

The reflection coefficient (analytical signal) was measured by depositing the organic reagent to the carrier surface, which further interacts with the metal ions to be determined. The advantages of this method are the increased selectivity of the reagent owing to the binding on the polymer matrix of the sorbent, and a possibility of immobilization of the water-insoluble organic reagents on a polymeric sorbent.

The absorption spectra of the iron complexes with immobilized reagents on a fibrous sorbent are consistent with their spectra in solution. The absorption maxima of the complexes formed in polyacrylonitrile matrix and in solution are virtually identical (Table 2). Identity of the spectra in solution and in the polymer phase indicates that the complex composition in polyacrylonitrile matrix (1:2) remains unchanged [13].

The high values of the distribution coefficient at the optimum sorption conditions allow efficient preconcentration and separation of the trace amounts of the determined element. Thus, the iron ions can be concentrated on the immobilized sorbent at acidic pH values.

Stability of the immobilized carriers in the strong electrolytes solutions (0.1 M NaCl) suggests that the binding of the organic reagent on a carrier is also due to the adsorption. The presence and decrease of the absorption bands at 3400–3500 cm^{-1} ($\Delta\nu$ 40–100 cm^{-1}) confirm the intermolecular hydrogen binding. The carrier is resistant to the strong acids and bases. The immobilized reagent can be desorbed (regenerated) after the treatment with 8.0 M solution of nitric acid. The carriers can be used up to 10–12 times.

The methods for iron determination by the developed express methodology was tested by the "added–found" procedure using model solutions (Table 3), simulating the real samples of natural waters, as well as using the real samples of water by comparison with the results obtained by means of the atomic absorption spectroscopy (Table 4). This confirms the suitability of the proposed method for the rapid analytical monitoring of natural waters.

EXPERIMENTAL

Reagents and apparatus. The standard solutions of iron(II, III) were prepared by dissolving the exact portions of Mohr's salt and ferric ammonium alum by the known procedures [14].

Table 2. Optimal conditions and analytical characteristics of the iron complexation ($n = 5$, $P = 0.95$)

Parameter	On the carrier	In aqueous medium
λ_{max}, nm	590	580
pH	2.5–3.5	3.0–4.0
ε, l mol^{-1} cm^{-1} [a]	1.5×10^4	1.4×10^4

[a] (ε) Molar absorption coefficient.

Table 3. Test results for the methodology for iron determination in the aqueous medium on the model solutions ($n = 5$, $P = 0.95$)[a]

Iron added, mg l^{-1}	Iron found, mg l^{-1}	S	S_{rel}
0.02	0.019±0.003	0.0012	0.064
0.04	0.041±0.004	0.0014	0.035
0.06	0.058±0.006	0.0021	0.035

[a] (n) Number of the parallel tests, (P) confidence level, (S) standard divergence, (S_{rel}) relative standard divergence.

Table 4. Test results for the methods of iron determination with IMPAR on the real samples of water ($n = 5$, $P = 0.95$)

Water samples	Iron added, mg l^{-1}	Iron found, mg l^{-1}	S	Iron found[a], mg l^{-1}
River	10.0	9.82	0.025	9.92
Waste water	10.0	10.01	0.028	9.89
Tap water	10.0	10.40	0.036	10.10

[a] Atomic absorption method.

The solution of disodium 1-(2-pyridylazo)-2-oxynaphthalene-3,6-disulfonate was prepared by dissolving a weighted sample in bidistilled water to the concentration of 1×10^{-3} M.

The buffer and the metal-containing solutions were prepared from the corresponding salts and acids of chemically pure or extra pure grade [15]. For the experiment the bidistilled water was used. The dilute solutions of the metals were prepared by diluting the stock solutions with bidistilled water prior to the experiment.

The required pH value was created with acetate-ammonia buffer solutions, pH of which was measured by an ionometer I-130 and pH meter pH/mV/TEMP Meter P25 Eco Met of a Korean production. The absorption spectra were measured on SF-46 and KFK-3 spectrophotometers, and the reflectance spectra, on a

Pul'sar colorimeter (OKBA Chemical Automation, Uzbekistan), recording the reflection spectra on 24 wavelengths in the visible range at the one flash of the pulse lamp. The IR spectra were registered on an Avatar 360 FT-IR spectrometer.

The fibrous materials synthesized as described in [10] were used as the carriers. The content of the reagent in the sorbent was determined spectrophotometrically from the change in optical density of the initial reactant solution at a maximum wavelength before and after the immobilization.

The characteristics of the immobilized reagent were determined in static mode. The disks with the immobilized organic reagent were placed in a beaker containing the studied solution and kept for some time under weak stirring. As the analytical signal we used the change in diffuse reflectance of the disks with the immobilized reagent.

The carriers were prepared as the discs of 2 cm diameter weighing 20–50 mg. The obtained disks were sequentially washed with 50 ml of 0.1 M HCl and 10 ml of acetone. Then the discs were placed into the beakers with 10 ml of the organic reagent with a concentration of 1.0×10^{-5}–1.0×10^{-3} M for 4–10 min, washed with 50 ml of distilled water and kept moist in Petri dishes.

Procedure for the iron determination in the water. In a 50 ml volumetric flask was injected the sample solution containing 2–50 mg of iron, then a buffer solution with a specific pH, 1.0 ml of 0.01 M of EDTA solution (to mask the mercury, copper, lead and other cations present in the waste water that interfere with the determined metal ions) were added and passed through an immobilized reagent on the carrier. The metal content was determined using a calibration curve constructed in the coordinates "reflection coefficient–concentration" $F = f(c)$.

Thus, we have developed a simple express method of sorption-spectroscopic determination of the iron(III) using an immobilized fiber reagent disodium 1-(2-pyridylazo)-2-oxynaphthalene-3,6-disulfonate and implemented it to analyze the samples of water of different nature.

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