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4-(8-Quinolylazo)resorcinol and 1-(8-Quinolylazo)-2-naphthol: Synthesis and Sorption Properties

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Absract—A methodology of the synthesis of 4-(8-quinolylazo)resorcinol (QAR) and 1-(8-quinolylazo)-2-naphthol (QAN) was developed. The synthesized compounds were used to modify an oxidized charcoal sorbent. The sorbent efficiently adsorbs copper(II) and zinc(II) cations to form surface electroneutral chelate complexes. The conditions of sorption and desorption of zinc(II) and copper(II) were studied.

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The demand for quantification of trace elements in different materials is constantly growing, especially for environmental monitoring purposes. Laboratories of water analysis use atomic emission and atomic absorption spectroscopy, photometry, fluorimetry, voltammetry, and potentiometry [1–3], which makes urgent the problem of preconcentration of samples before analysis. The progress of instrumental methods enhances requirements to concentration techniques and compatibility of the latter with the subsequent measurement techniques. The introduction of new instrumental methods not only does not restrict the scope of analytical approaches, but also prompts search for possibilities [4, 5].

The main methods of microelement concentration in water analysis include distillation, extraction, and sorption methods [6, 7]. Ion-exchange concentration offers certain advantages over other methods, including simplicity of implementation and possibility of group and individual elution of elements sorbed on the ion exchanger, using appropriate solvents. Considerable recent attention has been focused on modified charcoal sorbents, which are most commonly prepared by surface functionalization of charcoal [3, 8].

In the present work we synthesized 4-(8-quinolylazo)resorcinol and 1-(8-quinolylazo)-2-naphthol and used them for modification of a charcoal sorbent. Conditions of sorption and desorption of zinc and copper on the synthesized sorbent were studied with aim to assess its feasibility for sample preparation for atomic absorption or photometric analysis of water.

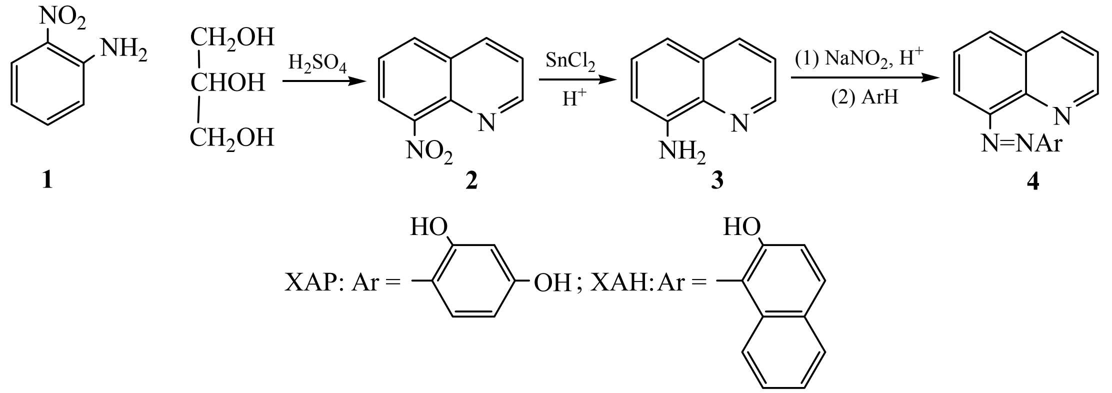
EXPERIMENTAL

4-(8-Quinolylazo)resorcinol (QAR) and 1-(8-quinolylazo)-2-naphthol (QAN) were synthesized by the Skraup condensation of 2-nitroaniline (**1**) with glycerol (**2**) followed by the reduction of the resulting 8-nitroquinoline (**3**) to 8-aminoquinoline (**4**), diazotization of the latter, and azo coupling of the diazonium salt that formed with resorcinol or 2-naphthol (see Scheme 1).

8-Nitroquinoline (3). Concentrated sulfuric avid, 385 mL, was slowly added to a suspension of 165.6 g (1.2 mol) of 2-nitroaniline (**1**) in 265 mL of water, the mixture was heated to the boil, and 125 mL (1.71 mol) of glycerol (**2**) was slowly added. The resulting mixture was refluxed under stirring for 4 h, cooled, diluted with equal volume of water, and neutralized with a 25% ammonia solution. The precipitate that formed was filtered off, washed with water, dried, dissolved in benzene, and chromatographed on alumina (Brockmann activity II) with benzene as eluent. The eluate was reduced in a minimal volume, 8-nitroquinoline was precipitated with methanol, filtered off, and dried at 70°C in air. Yield 75.6 g (72%).

8-Aminoquinoline (4). 8-Nitroquinoline, 30.0 g (0.17 mol) was added to a stirred solution 158.0 g

Scheme 1.



(0.7 mol) of $SnCl_2 \cdot 2H_2O$ in 200 mL of conc. HCl, the mixture was stirred for 1 h, and cooled with ice. The double salt of 8-aminoquinoline and $SnCl_2$, that precipitated, was filtered off, and decomposed by treatment of its cold solution with a solution of 50.0 g (1.25 mol) of NaOH with 200 mL of water. The mixture was stirred with cooling until the oil that separated had solidified, the solid was filtered off, washed with water, dried in air at room temperature, and recrystallized from petroleum ether. Yield 17.0 g (69%).

4-(8-Quinolylazo)resorcinol (QAR) and 1-(8-quinolylazo)-2-naphthol (QAN). A solution of 1.0 g (14.5 mmol) of $NaNO_2$ in 10 mL of water was slowly added to a stirred and cold (5°C) solution of 2.0 g (13.9 mmol) of compound **3** in 10 mL of 18% HCl. The mixture was stirred at 5°C for 30 min, and the resulting diazonium salt solution was slowly added to a stirred and cooled (≤15°C) to 1.5 g (13.7 mmol) of resorcinol (for QAR) or 2.0 g (13.9 mmol) of 2-naphthol (for QAN) dissolved in a mixture of 5.0 g (0.09 mol) of KOH and 20.0 mL of water. The mixture was stirred for 30 min and neutralized with acetic acid. The precipitates were filtered off, washed with water, and dried in air at room temperature and then at 90 °C for 2 h. Yield 1.8 g (50%) and 2.2 g (55%) for QAR and QAN, respectively.

Elemental analysis was performed on a Thermo Scientific FLASH EA 1112 CHNSO analyzer.

QAR: Found,%: C 67.8; H 4.3; N 15.7; O 12.2. $C_{15}H_{11}N_3O_2$. Calculated,%: C 67.92; H 4.15; N 15.85; O 12.08.

QAN: Found,%: C 76.0; H 4.5; N 13.9; O 5.6. $C_{19}H_{13}N_3O$. Calculated,%: C 76.24; H 4.38; N 14.04; O 5.35.

The electronic absorption (EA) spectra were measured on a Hitachi U-2000 scanning spectrophotometer in the range 400–800 nm. EA spectrum, λ_{max}, nm (log ε): QAN: 508 (4.34); QAR: 502 (4.28).

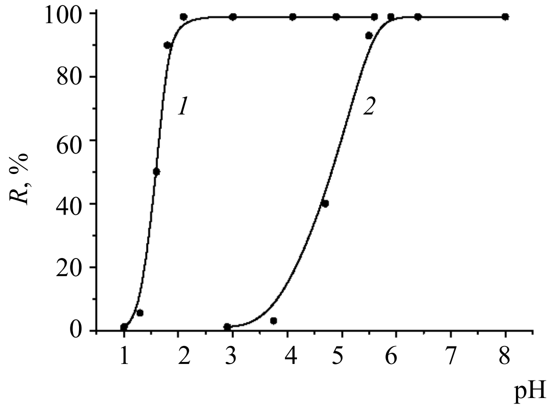
Surface oxidation of charcoal. A BAU-A activated charcoal (State Standard 6217-74) was refluxed for 30 min in 30% HNO_3. The oxidized sorbent was thoroughly washed with water to remove the acid [8] and poured with a 0.02% solution of QAN or QAR in ethanol. The suspension was refluxed with stirring for 6–8 h. The resulting materials were washed with ethanol and water. The concentration of the immobilized QAR (QAN) was estimated at 8–10 g per 1 kg of oxidized coal.

The concentrations of Cu(II) and Zn(II) ions were measured on a Carl Zeiss Jena AAS-3 flame atomic absorption spectrometer.

RESULTS AND DISCUSSION

The structures of QAR and QAN were calculated by the PM3 method using HyperChem 6.01 software. The calculations predicted a planar structure with the aromatic fragments trans to the aza bridge for both the aza compounds. The barrier to rotation of the quinolone fragment about the Naza-Ar bond is fairly low (20–25 kJ/mol).

The coordination of QAN and QAR with Cu(II) and Zn(II) ions is likely to stabilize those ligand conformations, where the donor oxygen and nitrogen atoms of the quinolone fragment and aza bridge are spatially proximate to each other. Evidence for this suggestion is provided by the fact that the EA bands of ethanolic solutions of the complexes are shifted red and slightly narrower compared to the respective bands



Dependence of the recoveries of (*1*) Cu(II) and (*2*) Zn(II) ions on pH for the QAR-modified oxidized activated charcoal. $c^0[\mathrm{M(AcO)_2}] = 0.3$ mg/L; $T = 298.15$ K.

of the ligands. As shown by the method of isomolar series, the complexes of QAN and QAR with Cu(II) and Zn(II) in ethanolic solutions have a 1 : 2 composition. At the same time, QAN and QAR immobilized on BAU-A activated charcoal were found not to adsorb Cu(II) and Zn(II) ions from aqueous solutions. Presumably, 1 : 2 cation–dye complexes do not form on the coal surface for steric reasons, whereas 1 : 1 complexes are not equilibrated by electrostatic forces. Aimed at improving the adsorption capacity of the modified sorbent, before treatment with QAN and QAR we oxidized the charcoal by the procedure in [5] to form ionogenic carboxylate groups on its surface.

The charcoal modified in this way efficiently adsorbs Cu(II) and Zn(II) cations. Obviously, the adsorption process involves both the surface carboxylate groups of the oxidized coal and the azo dye molecules. As a result, electroneutral chelate complexes with the possible composition coal–COO–M^{2+}–azo dye on the surface.

Table 1. Concentrations of zinc(II) on the surface of the BAU coal in dynamic conditions (pH = 6.5; V_{eluate} = 5 mL)

Volume, mL	Spiked, mg	Found[a], mg
25	0.100	0.090 ± 0.005
50	0.100	0.110 ± 0.003
100	0.100	0.100 ± 0.003
200	0.050	0.130 ± 0.005
200	0.025	0.052±0.003
200	0.050	0.023±0.003
200	0.010	0.009±0.003

[a] Averaged over 5 runs.

Adsorption of Cu(II) and Zn(II) cations was performed at 298.5 ± 0.1 K from buffer solutions of their acetates in dynamic conditions, by passing solutions with concentrations 0.1–5 mg metal/L through sorbent-packed columns (length 50 cm, diameter 2 cm) at a rate of 1–15 mL/min. The amounts of the adsorbed ions were estimated by eluting them with 10% HCl and analyzing the eluates by atomic adsorption spectroscopy. The optimal eluent flow rates were 8–10 mL/s; in this case, 99–100% recoveries of copper and zinc could be obtained at certain pH values. Quantitative adsorption of Co(II) and Zn(II) was observed at pH > 2 and pH > 8, respectively (see figure). The Co(II) and Zn(II) adsorption capacity of the synthesized sorbents is 0.18–0.20 mg-equiv/g.

The QAR-modified sorbent provides quantitative adsorption of metal ions even if the concentrations of the latter in the solutions are fairly low, as illustrated in Table 1 on an example of zinc ions.

The possibility of multiple use of the sorbent was studied in dynamic conditions. In was shown that after 50 runs the Zn(II) adsorption capacity was 95% of the initial capacity.

The data in Table 2 illustrate the high accuracy of reproducibility of the determination of metal ions in model solutions with the use of the QAR-modified BAU coal sorbent.

Thus, the use of the modified coal in the analysis of aqueous solutions allows almost complete extraction of metals from the matrix, which is quite important for their subsequent atomic adsorption determination.

The results of the present research were used to develop the following procedure of the concentration

Table 2. Determination of Zn(II) and Cu(II) in model solutions by atomic absorption spectroscopy with preconcentration on a modified BAU coal

Metal	Spiked, mg/L	Found[a], mg/L
Copper	0.015	0.015 ± 0.002
	0.010	0.011 ± 0.002
	0.005	0.005 ± 0.001
Zinc	0.015	0.015 ± 0.003
	0.010	0.009 ± 0.003
	0.005	0.004 ± 0.001

[a] Averaged over 5 runs.

of metal ions from water: 200 mL of a water sample with pH 6–8 [for Cu(II)] or 8–10 [for Zn(II)] is passed at a rate of 5–10 mL/min through a chromatographic column packed with the modified activated coal, 5 mL of 10% HCl is then passed at a rate of 1–1.5 mL/min, and the concentration of metal ions in the eluate is measured by atomic absorption spectroscopy.

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