

Application of Amberlite XAD resins to the isolation of humic substances from sea water*

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Humic substances
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Abstract

XAD-2 and XAD-8 resins were found to be equally efficient as sorbents of dissolved humic substances from sea water but the substances sorbed on the former were found more difficult to elute. UV-VIS and IR spectra of the isolated humic substances did not differ significantly, indicating the affinity of both resins to the same range of substances.

The influence of desorbents (solutions of NH_4OH and NaOH) on the quality of the substances was tested. After removal of excess base by vacuum evaporation (NH_4OH) and ion exchange (NaOH), a higher level of nitrogen was found in the humic acids eluted with ammonium hydroxide, a fact attributable to the formation of ammonium salts of the humic substances. Irreversible sorption on the ion exchanger was the reason for the smaller proportion of the high molecular weight fraction in the substances eluted with sodium hydroxide.

1. Introduction

Sorption on solid sorbents has been proved a convenient and effective way of isolating humic substances from aqueous solutions (Sieburth and Jensen, 1968; Aiken, 1985). A variety of sorbents, including nylon, activated carbon and the C-18 reverse phase, has been applied to this end.

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In recent years nonionic macroporous Amberlite XAD resins have become the most popular sorbents (Mantoura and Riley, 1975; Stoumer and Harvey, 1977; Aiken *et al.*, 1979; Pempkowiak *et al.*, 1979). The most frequently used XAD-2 and XAD-8 resins have similar mechanical properties (pore diameter, surface area) but their matrices are entirely different: XAD-2 is a hydrophobic copolymer of styrene-divinylbenzene, while XAD-8 is a crosslinked aliphatic polymer (acrylic ester) with a more hydrophilic structure (Anon., 1972). This difference may lead to the isolation of different fractions of dissolved organic matter with respect to both quantity and quality. Therefore to compare results on humic substances isolated using various resins seems irrelevant unless the effectiveness of isolation and some of the properties of the substances isolated from the same water sample are proven similar.

The aim of this work was to examine the efficiency of both resins as sorbents of humic substances from brackish water, to compare selected properties of the substances obtained and to determine the influence of the isolation procedure on their quality.

2. Experimental

Samples of water from the Gulf of Gdańsk were collected in polyethylene barrels, filtered (precombusted Whatman GF/C filters), acidified to pH = 2 (concentrated HCl) and pumped through glass columns filled with Amberlite XAD-2 and XAD-8 resins. The dimensions of the resin bulk were 30 cm × 3 cm², the water flow rate 10 cm³ min⁻¹.

The resins were purified before use by Soxhlet extraction with methanol and acetone, then packed into columns and rinsed continuously with redistilled water until no absorbance at 220 nm (1 cm cell) of the water flowing through could be detected.

After 300 dm³ of the sea water had been passed through the columns, these were flushed with deionized water until no chloride ions were detectable (AgNO₃ test). The sorbed substances were eluted with 0.1 M NaOH or 0.5 M NH₄OH. The excess ammonium hydroxide was removed by vacuum evaporation at 50°C, and the extract containing NaOH was desalinated by being passed through a Regin 101 (H⁺) ion exchanger. The concentrations of the substances in the resulting solutions were determined gravimetrically. The A_{4/6} coefficient (the ratio of absorbances at 465 nm and at 665 nm) was calculated after the absorbances of the solutions had been measured in a Specord (Zeiss, Jena) spectrophotometer. The molecular weight distribution was determined by ultrafiltration carried out in a stirred, pressurized ultrafiltration cell (Amicon) with Diaflo-type membranes.

3. Results and discussion

The tested resins differ significantly with regard to ease of purification. While distilled water passing through the XAD-8 resin (which had undergone a 24-hour Soxhlet extraction) showed no detectable absorbance, the XAD-2 resin required an additional 16 h extraction. However, this finding may apply only to previously unused resins: it has been observed that the level of bleeding from XAD-2 resin decreased with the time of its use (Daignault *et al.*, 1988).

In order to estimate sorption efficiency and ease of desorption, resins were eluted with the base solution during the course of six days. The solution in which the resins were soaked was replaced every 24 hrs. Eluant absorbances are given in Table 1.

Table 1. Absorbance of humic acid solutions desorbed from XAD-2 and XAD-8 resins by means of 0.1 M NaOH (absorbance at 665 nm in 1 cm cell)

Resin type	Day of elution						Σ^*
	1st	2nd	3rd	4th	5th	6th	
XAD-2	0.43	0.35	0.20	0.12	0.05	0.05	1.20
XAD-8	0.68	0.20	0.08	0.05	0.03	0.02	1.14

* denotes the sum of absorbances.

Assuming that absorbance is proportional to concentration (volumes of solutions are the same), the sorption and desorption efficiencies of the two resins can be considered similar. However, desorption from the XAD-8 resin is faster and more thorough. Small though it may seem, this difference could be important: apart from the time factor, a fraction of humic substances is irreversibly sorbed on XAD-2 and therefore lost to further analysis.

Table 2 presents the results of the qualitative analysis of the humic substances desorbed from XAD-2 and XAD-8 resins by means of 0.1 M NaOH and desalinated by ion exchange.

The figures in Table 2 prove that both resins absorb substances of similar characteristics.

The desalination step is necessary because the eluates contain an excess of base. Gravimetric analysis revealed that up to 30% of humic substances were irreversibly sorbed on the ion exchanger. This loss can be avoided if ammonium hydroxide is applied instead of sodium hydroxide.

Table 2. Properties of the humic substances isolated by means of 0.1 M NaOH

Resin type	Elemental composition (%)				A _{4/6} *
	ash	C	H	N	
XAD-2	6.0	46.3	5.1	2.3	5.3
XAD-8	5.9	47.2	5.3	2.3	5.1

Resin type	IR spectra		Molecular weight (%)	
	1710 cm ⁻¹	1390 cm ⁻¹	fraction < 5000 D	5000 D < fraction < 10000 D
XAD-2	strong	weak	93.0	2.5
XAD-8	strong	weak	95.0	1.5

* ratio of absorbances at 465 nm and 665 nm.

The excess NH₄OH can be removed by vacuum evaporation. The analysis of the substances thus obtained yielded the following results:

- elemental composition (%): ash - 2.9; C - 48.2; H - 4.8; N - 4.6,
- IR spectrum: 1710 cm⁻¹ - weak; 1390 cm⁻¹ - weak,
- A_{4/6}: 4.2,
- molecular weight (%): fraction < 5000 D - 80.1; 5000 D < fraction < 10000 D - 13.5.

In comparison with the data in Table 2, the ash content decreased by 50% and the nitrogen content increased by 40%. The latter fact indicates that ammonium salts of humic acids are obtained instead of protonated acids. This conclusion is supported by the decrease in absorption of the 1710 cm⁻¹ band which occurs upon neutralization of humic acids (Theng *et al.*, 1967). The larger content of the high molecular weight fraction confirms the possibility that some substances may be lost from the solution while being passed through the ion exchanger.

4. Conclusions

Humic substances isolated by means of both XAD-2 and XAD-8 resins are of similar quantity and quality. However, not only does the 'aromatic' XAD-2 resin require a longer purification process, it is also more difficult to elute. An insufficient elution time may result in the incomplete desorption of humic substances. The use of NH₄OH solution as desorbent is discouraged because of its possible influence on the elemental composition of the substances isolated. However, the desalination of the NaOH solution on the ion exchanger leads to the partial loss of the high molecular weight fraction.

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