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SYNTHESIS OF MACROPOROUS ELLAGITANNIC ACID RESIN AND ITS CHELATING PROPERTIES FOR METAL IONS

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ABSTRACT

A new type of macroporous ellagitannic acid resin (EAR) can be prepared from macroporous crosslinked chloromethylated polystyrene beads and ellagic acid in the presence of NaOH and KI as catalysts. The synthetic route and structure of the polymer were examined. The structure of EAR was confirmed by elementary analysis and IR spectra. The oxygen content of EAR was 7.06%, and the functional group capacity of EAR was 0.441 mol EA/g EAR. The conversion of functional groups was 8.33%. Cu^{2+}, Fe^{3+}, Ce^{3+}, and La^{3+} can be easily adsorbed by EAR. The adsorption capacities for these metal ions per g EAR were 0.609 mmol Cu^{2+}, 1.523 mmol Fe^{3+}, 0.320 mmol Ce^{3+}, and 1.561 mmol La^{3+}. The influence of pH, acidity, ionic concentration, adsorption time, and temperature on the percentage of adsorption was investigated.

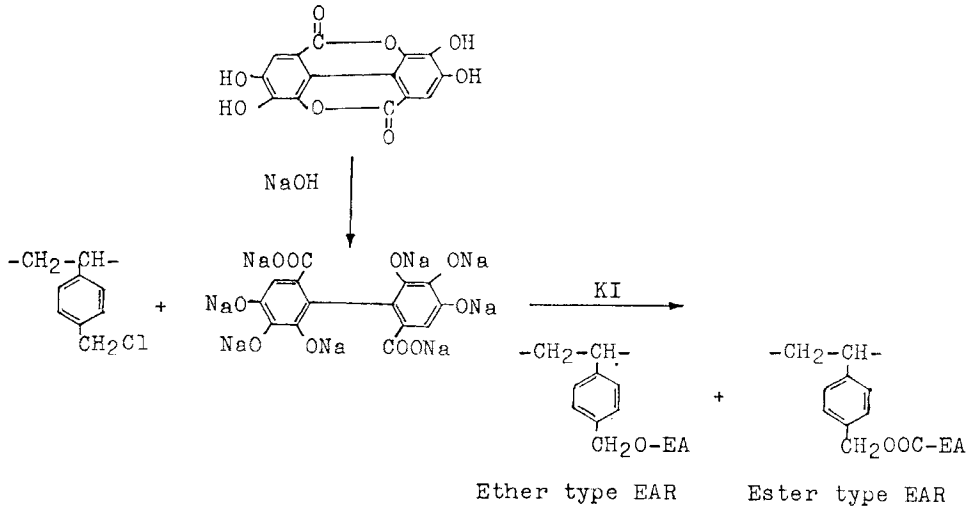
INTRODUCTION

Natural humic acid contains polyphenolic hydroxy and carboxylic groups, and many metal ions can be chelated by it. The synthesis of macroporous humic acid resins and their chelate properties for heavy-metal ions have been reported by us [1, 2].

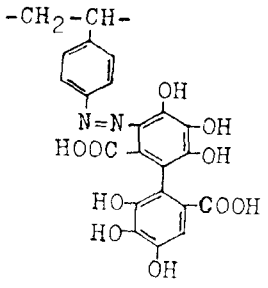
Ellagitannic acid (EA) and ellagic acid, which can be separated from natural tanning material, also contain polyphenolic hydroxy, carboxylic, and internal ester groups. Ellagitannic acid, ellagic acid, and their metal complexes exhibit many characteristic properties, such as ultraviolet spectra, absorption of oxygen, and anticorrosion, reducing, catalytic, antifungal, and some pharmacological properties.

Ellagic acid is easy converted into ellagitannic acid with alkali. Since ellagitannic acid contains hexaphenolic hydroxy and dicarboxylic groups, it has good chelate properties for metal ions.

According to the following reaction, macroporous ellagitannic acid resin (EAR) can be prepared from macroporous crosslinked chloromethylated polystyrene beads and ellagic acid in the presence of NaOH and KI as catalysts:



Azo-type ellagitannic acid resin can be synthesized from macroporous polystyrene beads (PS) by nitration, reduction, diazotization of PS, and coupling of the diazonium salt of the polystyrene beads with the ellagitannic acid.



Azo-EAR

Under the conditions used for the humic acid resins, the chelate properties for metal ions of the ether/ester-type humic acid resin were better than those of azo-type humic acid resin; hence our interest in ether/ester-type EAR.

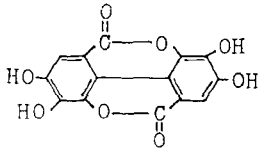
In this paper the structure of EAR is confirmed by elementary analysis and IR spectra, the percentage of conversion of functional groups is reported, and the chelate properties of EAR for Cu^{2+}, Fe^{3+}, Ce^{3+}, and La^{3+} are studied.

EXPERIMENTAL

Materials

Crosslinked chloromethylated polystyrene beads, macroporous type; degree of crosslinking, 6%; divinylbenzene, chlorine content 21.65%; specific area, 13.0 m^2/g (determined by Carlo Erba Strumentazione Sortomatic Mod Series 1800).

Ellagic acid: MW 302.19, black powder.



Elemental Analysis

	C, %	H, %	O, %
Observed	54.27	1.99	43.74
Calculated	55.64	2.00	42.36

Ellagic acid in ethanol, λ_{max} 367-368 and 253.5-254.5 nm (determined by UV 210A photometer). Literature values [3]: 366 and 255 nm.

The other reagents were of analytical reagent or chemically pure grade.

Synthesis of Macroporous Ellagitannic Acid Resin

The synthetic conditions of EAR were the optimum conditions for ether/ester-type humic acid resin described previously [1, 2]. The ratio of ellagic acid:chloromethylated polystyrene:sodium hydroxide:potassium iodide:H_2O were 5:2:1:1.5:125 (by weight) and 1.35:1:2.00:0.74:563 (molar).

After swelling the macroporous crosslinked chloromethylated polystyrene beads in DMF, the excess swelling agent DMF was removed by suction filter. The swollen chloromethylated polystyrene beads were added to an aqueous solution of ellagic acid, sodium hydroxide, and potassium iodide according to the above-mentioned ratio, and then the reaction mixture was reacted at 80°C for 60 h with stirring under nitrogen. After filtration, the resin was washed with a large amount of deionized water, methanol, and ether, successively. EAR was dried at 50°C under vacuum.

Determination of the Chelate Properties of EAR for Some Rare-Earth Ions and Metal Ions

Photometric Determination of Ce^{3+}, La^{3+}, and Fe^{3+}

The calibration curve for Ce^{3+} and La^{3+} was determined by the Arsenazo III [2,7-bis-(20arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] method [4], while that for Fe^{3+} was made by the thiocyanate method [5].

Procedure for Ce or La. Transfer a solution containing 20-100 μg Ce^{3+} or La^{3+} into a 50-mL volumetric flask, add 2 mL 1% ascorbic acid solution, 1 mL formic acid buffer solution, 4 mL of 0.05% Arsenazo III solution, and dilute with water to the mark, pH 2.6 (± 0.1). A solution containing 4 mL of 0.05% Arsenazo III and 1 mL buffer, total volume 50 mL, is used as the standard. Measure the absorption of the solutions at 650 nm on a 751-G UV-spectrophotometer.

Procedure for Fe^{3+}. Determine thiocyanate photometrically under the following conditions: less than 70 μg Fe^{3+}, 10 mL of 20% KSCN solution, total volume 50 mL, with the solvent as the standard at 495 nm.

Determination of Cu^{2+}

EAR (68.0 mg) and 0.01 *N* $CuSO_4$ (50 mL). Shake for 24 h and then titrate the residual Cu^{2+} in the aqueous solution with standard $Na_2S_2O_3$ solution.

RESULTS AND DISCUSSION

1. Structure of EAR

The UV spectra of ellagic acid in the 380-180 nm range show absorption bands at 253.5-254.5 and at 367-368 nm, which are probably due to aromatic carboxyl and hydroxy groups of ellagic acid.

$PSCH_2Cl$ has a band at 670 cm^{-1}, which is characteristic of C–Cl, and a band at 1260 cm^{-1} that can be assigned as the nonplanar wagging of $-CH_2-$ [4]. The bands at 670 and 1269 cm^{-1} in EAR disappear, and new bands appear at 1685 cm^{-1} (–COOH), at 1365 and 1340 cm^{-1} (phenolic OH), and at 1180 and 1100 cm^{-1}, which can be attributed to the newly formed aromatic ether and ester linkages, respectively.

2. The Functional Group Conversion of the Resin

The chlorine content of macroporous crosslinked polystyrene beads was 21.65%, which is equivalent to 6.1 mmol Cl/g $PSCH_2Cl$ resin.

The oxygen content of the ellagitannic acid resin, both of the ester type and the ether type, was 7.06%, which is equivalent to 0.441 mmol ellagitannic acid in the ellagitannic acid resin. Thus, the functional capacity of EAR is 0.441 mmol EA/g EAR, and the conversion of functional groups equals 8.33%.

3. Influence of pH and Acidity on the Adsorption of the Various Metal Ions

The influence of pH and acidity on the adsorption, i.e., chelating, properties of Fe^{3+}, Ce^{3+}, and La^{3+} were examined (Fig. 1). The data show that, in the 3-5 pH range, the adsorption on the resin of Fe^{3+} and La^{3+} was higher, but the adsorption of Ce^{3+} at pH 3-4 was lower. The optimum pH values for adsorption of Fe^{3+} and La^{3+} are 5 and 4, respectively, as shown in Fig. 1.

4. Influence of Ionic Concentration on Adsorption

As shown in Fig. 2, the adsorption of Fe^{3+}, Ce^{3+}, and La^{3+} increased with ionic concentration.

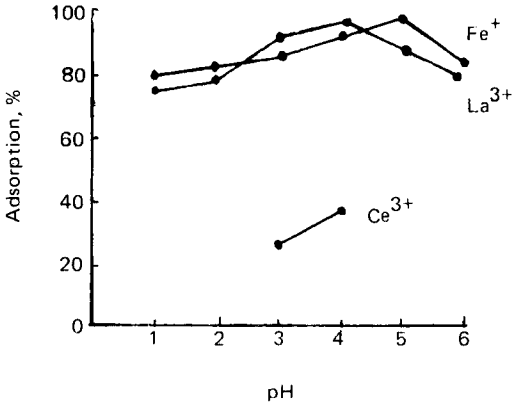


FIG. 1. Influence of pH on adsorption of various metal ions. Ion 1.0 mg, total volume 10 mL, EAR 100 mg, shaking at 20°C for 8 h.

5. Influence of Time on Adsorption

The adsorption increased rapidly with time and then reached an equilibrium (Fig. 3). If the resin is fully swollen before use, the rate is faster.

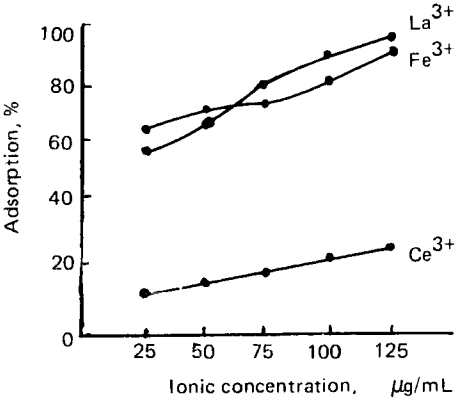


FIG. 2. Influence of ionic concentration on adsorption. EAR 100 mg, total volume 10 mL, pH 4.0, shaking at 20°C for 1.5 h.

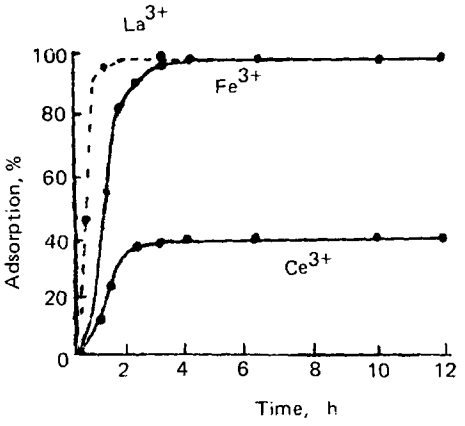


FIG. 3. Influence of time on adsorption. pH 4.0, other conditions as in Fig. 1. (—) Dry resin. (- -) Swollen resin.

6. Influence of Temperature on Adsorption

The adsorption decreased slowly with increasing temperature, as shown in Fig. 4.

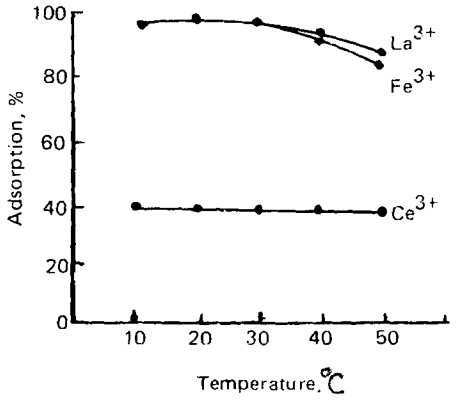


FIG. 4. Influence of temperature on adsorption. pH 4.0, shaking for 5 h, other conditions as in Fig. 1.

7. Adsorption Capacities and Distribution Coefficients for Various Metal Ions on EAR

The adsorption capacities per gram EAR are 0.609 mmol Cu^{2+}, 1.523 mmol Fe^{3+}, 0.320 mmol Ce^{3+}, and 1.561 mmol La^{3+}.

The adsorption ability may be expressed in terms of the distribution coefficient K_d [7], which was determined under the following conditions: EAR 100 mg; Fe^{3+}, Ce^{3+}, and La^{3+} 20 mmol; 10 mL; shaking for 24 h; Cu^{2+}: EAR 68 mg, 0.01 *N* $CuSO_4$ 50 mL. The results were as follows: La^{3+} (353) > Fe^{3+} (319) > Cu^{2+} (146) > Ce^{3+} (19).

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