Indian Journal of Chemistry
Vol. 28A, December 1989, pp. 1128-1129

Sorption behaviour of carboxylic acids on zirconium(IV) selenophosphate

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Received 7 February 1989; revised and accepted 17 April 1989

The sorption behaviour of carboxylic acids on zirconium(IV) selenophosphate has been evaluated by batch and column methods. In the column experiments, zirconium(IV) selenophosphate shows a quantitative collection of carboxylic acids at low concentrations.

The increasing concern for the protection of water quality has led to the development of new analytical methods for potentially hazardous water pollutants[1]. Various organic pollutants exist at relatively low concentrations in water; therefore, these are concentrated before their qualitative and quantitative analysis. Low molecular weight carboxylic acids pose significant problems in standard wastewater treatment operations, such as solvent extraction, powdered activated carbon treatment and biological treatment[2]. The clean-up of waste water containing these constituents requires expensive operations such as wet-air oxidation[3]. Without such clean-up, a high level of dissolved organic carbon may result which violates permit regulations. In addition, the presence of these compounds may increase the water solubility of the non-polar pollutants[4]. These compounds have also been shown to exhibit biological activity either by acting as a carbon source for microbial growth, or by exhibiting toxicity[5]. The probability of finding these compounds in certain aqueous systems is high[4,6]. For the purpose of concentration of low-level organic pollutants, some commercially available porous polymer sorbents like Amberlite XAD[7,8], Tenax GC[7], Separon[9] and Hitachi gel[10] have been widely used. The sorption behaviour of aromatic compounds in water on β-cyclodextrin polyurethane resins has been studied[11] and found suitable for the qualitative collection of aromatic compounds at low concentrations.

In this note, we describe the sorption behaviour of carboxylic acids on zirconium(IV) selenophosphate ion exchanger. The column of zirconium(IV) selenophosphate has been used as a sorbent to concentrate some carboxylic acids in artificial water samples.

Experimental

Zirconium(IV) oxynitrate (BDH), sodium selenite (BDH) and orthophosphoric acid (BDH) were used for the synthesis of ion-exchange material. All the other chemicals and reagents were of analytical grade.

A Bausch and Lomb Spectronic 20 colorimeter and Elico model Li-10 *p*H meter were used for spectrophotometric studies and *p*H measurement respectively.

Synthesis

Zirconium(IV) selenophosphate ion-exchanger[12] was synthesized by adding an aqueous solution 0.05 *M* in sodium selenite and 0.05 *M* in orthophosphoric acid to an aqueous solution of zirconium(IV) oxynitrate at *p*H 1. The gel so formed was allowed to settle for 24 hr, washed with demineralized water to remove excess reagents and finally filtered under suction. It was then dried at 40°C. The dried material was treated with demineralized water so as to convert the exchanger into smaller particles. This treatment was exothermic in nature. The material was first converted into H^+-form and then converted to Ag^+-form by keeping it in 0.10 *M* $AgNO_3$ solution.

Procedure

Capacities of zirconium(IV) selenophosphate exchanger in Ag^+-form for sorption of carboxylic acids were determined by the batch method. A mixture of 250 mg of the exchanger material and 50 ml of an aqueous solution containing carboxylic cid (0.4 mmol, $pH \leqslant 3$) was kept in an Erlenmeyer flask for 24 hr to allow attainment of equilibrium. The exchanger material was then removed by filtration. The concentration of the solute in the filtrate was determined spectrophotometrically using sodium metavanadate as a colouring reagent[13] for all the carboxylic acids studied except α-ketoglutaric acid, sulphosalicylic acid, salicylic acid and ascorbic acid which were determined using dinitrophenylhydrazine, ferric chloride and silicomolybdic acid respectively[14,15]. From this value the sorption capacity (mmol g^{-1} exchanger) was calculated.

The column experiments were carried out using a 0.6 cm (i.d.) glass column packed with 2.0 g of exchanger, zirconium(IV) selenophosphate, (50-100 mesh) in Ag^+-form. Each acid sample (50 ml) was passed through the column at a flow rate of 1 ml min^{-1}.

Results and discussion

The sorption capacities of zirconium(IV) selenophosphate in Ag^+-form for the carboxylic acids by batch system are given in Table 1. The results of these studies suggest that citric acid is strongly sorbed on the material while salicylic acid is not sorbed at all. The decreasing order of sorption capacities for various acids is as follows: citric acid > propionic acid > malic acid > acetic acid > benzoic acid > maleic acid > α-ketoglutaric acid > oxalic acid > phthalic acid > formic acid > succinic acid > tartaric acid > ascorbic acid > sulphosalicylic acid.

The sorpiton capacity for benzoic acid on zirconium(IV) selenophosphate in Ag^+-form is also higher than those on Amberlite XAD-2 and Amberlite XAD-7[11].

The results of uptake of carboxylic acids by zirconium(IV) selenophosphate in Ag^+-form by column method are given in Table 2. The material in Ag^+-form shows a complete quantitative collection of citric acid, propionic acid, malic and maleic acid at these low concentrations. However, the per cent uptake of benzoic acid, phthalic acid and succinic aid decreases as the concentration of the solute increases. These results suggest that zirconium(IV) selenophosphate in Ag^+-form can be used satisfactorily as a sorbent to collect carboxylic acids present at low concentrations in water.

Table 1 – Sorption capacities for carboxylic acids on zirconium(IV) selenophosphate in Ag^+-form at 25 ± 2°C

Solute[a]	Sorption capacities (10^{-2} mmol g^{-1} exchanger)
Formic acid	8.2
Acetic acid	11.8
Citric acid	14.0
Propionic acid	12.2
Malic acid	11.9
Maleic acid	10.8
Phthalic acid	8.6
Succinic acid	7.9
Oxalic acid	8.7
Tartaric acid	7.2
Salicylic acid	0.0
Sulphosalicylic acid	2.8
Benzoic acid	11.2
Ascorbic acid	6.8
α-Ketoglutaric acid	9.1

[a] Concentration of solute = 0.4 mmol

Table 2 – Per cent uptake of carboxylic acids by column method

Solute	Concentration (mmol)	Uptake (%)
Citric acid	0.01	100
	0.05	100
Propionic acid	0.01	100
	0.05	100
Benzoic acid	0.01	90
	0.05	81
Phthalic acid	0.01	100
	0.05	69
Malic acid	0.01	100
	0.05	100
Maleic acid	0.01	100
	0.05	100
Succinic acid	0.01	90
	0.05	84

Acknowledgement

We are thankful to Prof. S.M. Osman, Chairman, Department of Chemistry for facilities.

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