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USE OF ADSORBENTS FOR RECOVERY OF ACETIC ACID FROM AQUEOUS SOLUTIONS
PART III -- SOLVENT REGENERATION

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ABSTRACT

Solvent leaching was investigated as a method of regeneration for activated carbons and polymer sorbents loaded with acetic acid by contact with aqueous solutions. Both batch-equilibration and fixed-bed experiments were employed. Methanol, methyl acetate, and acetone are suitable regeneration solvents for most activated carbons. Amoco GX-031 is an exception, giving incomplete regeneration. Methanol provides still more efficient regeneration for macroreticular styrene-divinylbenzenes adsorbents. Among basic sorbents, amine resins give incomplete regeneration by solvent leaching, as does a poly N oxide. Polybenzimidazole, a weaker base, gives higher recoveries of acetic acid when leached by solvents. Poly(4-vinylpyridine) is regenerated completely and efficiently by methanol, methyl acetate, and acetone in a fixed-bed geometry. It thus appears that an intermediate degree of basicity is desirable in a synthetic sorbent for acetic acid -- strong enough to give the

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* - Present Address: Millipore Systems Division, South San Francisco, CA 94080

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INTRODUCTION

In a process for recovering a solute from aqueous solution it is necessary to reclaim the product solute from the adsorbent. Furthermore, in order for the process to be economical, it is important for the adsorbent to be regenerated to a form where it can be reused, with little or no loss of capacity or need for replacement over many cycles.

The most commonly used approach for regeneration of adsorbents is stripping at a higher temperature and/or lower pressure. This approach requires that the solute be sufficiently volatile. Furthermore, for a bulk recovery process where the solute loading is necessarily high, the cost of heating and/or vacuum stripping is substantial. Leaching of the adsorbate with a solvent affords an alternative route. Even for the more volatile solutes, such as acetic acid and phenol[1], regeneration by solvent leaching is usually more attractive economically than regeneration by volatilizing the solute, at the concentrations of aqueous feed solution that are suitable for solute-recovery processes and at the adsorbent loadings that are economically desirable.

Although there are some published data on regeneration of carbons by solvent leaching after adsorption of phenol[2,3], there has been little published on solvent leaching for regeneration of other adsorbed solutes. The purpose of the present work was to identify the most favorable solvents for recovery of adsorbed acetic acid from activated carbons and polymer sorbents, to ascertain the approximate amounts of solvent that would be required, and to observe any fractionation between acetic acid and co-adsorbed water that would occur during regeneration.

The most likely solvents to be used are ones that are themselves volatile and do not strongly attach to the adsorbent or sorbent. These properties are desirable so that the residual solvent can be economically removed by a means such as steam stripping before the adsorbent is reused.

Only simple leaching by solvent liquids is reported here. There are opportunities for further improving on the regeneration process. Some of these are the following:

1. Use of a regeneration solvent which is also an effective entrainer for a subsequent azeotropic distillation of the leachate (solvent, solute, and water), in which the water is preferentially volatilized in the presence of the entrainer. This approach parallels the method used commercially for recovery of acetic acid from aqueous solution by solvent extraction [4,5]. If the solvent is less volatile than the solute, there is an analogous possibility where the presence of the solvent serves as the solvent for an extractive distillation in which water is preferentially volatilized.

2. Use of a vaporized regeneration solvent which carries out the same sort of azeotropic distillation directly on the adsorbent bed[6].

3. Use of an adsorbent which is also an effective esterification catalyst[6,7]. This enables an adsorbed carboxylic acid to be esterified directly on the adsorbent bed. The ester is less strongly adsorbed than the

carboxylic acid and may be more volatile, thereby facilitating regeneration by either solvent leaching or volatilization. Also, the ester may be the desired product.

Two basic methods were used to evaluate solvents for regeneration. One was batch equilibration, similar to that described in Parts I and II, but involving contact of a loaded adsorbent with the solvent in a controlled ratio. The second method was fixed-bed regeneration, with the apparatus and procedure the same as already described in Part II, with typical results shown in Figure 8 of Part II.

RESULTS AND DISCUSSION

Solvent Regeneration of Carbons

Table I reports results of a series of experiments wherein Witcarb 950 was contacted with a number of different solvents in closed flasks in a shaker bath for several hours, a period of time after which no further discernible changes occurred. The carbon had been equilibrated with a raffinate containing 3.23% (w/w) acetic acid in water. The weight ratio of solvent to wet carbon was 5.0, and the acetic acid uptake was 0.195 g/g dry carbon. The adsorbate contained about 2.1 g H_2O/g acetic acid, and the weight ratio of wet to dry carbon was 1.57. Acetic acid and water concentrations in solution were measured by gas chromatography. Both % recoveries of acetic acid and weight ratios of water to acetic acid removed are reported. A ratio of water to acetic acid removed above 2.1 corresponds to preferential removal of water, while a ratio below 2.1 corresponds to preferential removal of acetic acid. When two liquid phases developed, the results are for the combination of the two. The results are averages from at least two duplicate measurements, with scatter of order 10%.

TABLE I.

Regeneration of Witcarb 950 with Various Solvents

Solvent	% Recovery of of Acetic Acid	Wt. Ratio of Water to Acetic Acid Extracted
Acetone	100	1.9
Methyl Acetate	100	2.5
Ethyl Acetate	94	1.2
n-Propyl Acetate	94	1.3
Methanol	89	--
n-Butyl Acetate	84	0.94
Methyl Ethyl Ketone	82	--
Dimethyl Sulfoxide	82	3.0
Toluene	56	0.47
Diisopropyl Ether	38	0.72
Undecane	10	0.39

From Table II, methyl acetate, methanol, and acetone are the most effective volatile solvents for recovery of acetic acid. The capacity for acetic acid drops excessively for solvents which remove acetic acid selectively over water, with the exceptions of ethyl, propyl and butyl acetates. However, it was found to be difficult to remove these latter solvents for reuse of the carbon, in part because of their immiscibility with water.

In another series of experiments Norit Row 0.8S carbon was used and reused several times for adsorption of acetic acid from aqueous solution, with batch regenerations by methanol in between. There was no noticeable loss of capacity. However, only about 50% of the acetic acid adsorbed by Amoco GX-031 carbon could be removed by repeated batch contactings with methanol. Acetone removed about the same fraction or less, and even tributyl phosphate (a much stronger Lewis base) recovered only

TABLE II.

Results of Fixed-Bed Regenerations of Activated Carbons and Non-Functionalized Macroreticular Polymers

[In all cases, aqueous feed contained 5% acetic acid, bed volume was 26.5 mL of adsorbent, and regenerant flow rate was 1.0 mL/min, except where noted.]

Adsorbent	Regenerant	Maximum % (w/w) Acetic Acid in Regenerant	Regenerant Volume for 90% Recovery of Acetic Acid (mL)
Carbons			
Witcarb 950	Methanol	12	45
	n-Butyl Acetate	8	Large*
G-BAC	Methanol	16	40
	Methyl Acetate	18	35
Witco Columbia	Methyl Ethyl Ketone	7	90
	Acetone	9	(90)
Non-Functionalized Polymers			
XAD-4	Methanol	12	25
100% Poly(DVB)	Methanol	5.5**	15**
Basic Polymers			
Dowex WGR	Dimethyl Sulfoxide	2	***
Reilly PVP	Methanol	15	30
	Acetone	12	35
	Methyl Acetate	10	40

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* - 30% recovery in 60 mL regenerant volume.

** - Aqueous feed contained 2.6% (w/w) acetic acid; regenerant flow rate substantially higher than 1.0 mL/min, but unrecorded; these changes account for the relatively low maximum acetic acid concentration in the regenerant.

*** - 26% recovery in 40 mL of regenerant volume.

42% of the acetic acid. Apparently the very fine pores of Amoco GX-031 either swell in these solvents, are otherwise inaccessible to the solvent, or adsorb irreversibly. This difficulty was not encountered with other carbons.

Fixed-bed adsorption-regeneration experiments were carried out with methanol regeneration of acetic acid and water from Witcarb 950 and Union Carbide G-BAC, methyl acetate regeneration of G-BAC, and n-butyl acetate regeneration of Witcarb 950[8]. The result for methanol regeneration of Union Carbide G-BAC carbon is shown in Figure 8 of Part II. Similar measurements were also made for regeneration of Witco Columbia carbon with methyl ethyl ketone and acetone. In all cases, the aqueous feed contained 5% (w/w) acetic acid. Approximately 55 mL of aqueous effluent left the bed before breakthrough began during the loading half-cycle, and breakthrough was complete at about 85 mL. Table II reports the maximum acetic acid concentration obtained in the regeneration effluent and the regenerant volume required for elution of 90% of the acetic acid, for these and other fixed-bed runs. There was only a small amount of fractionation between acetic acid and water during regeneration. Methyl acetate is a somewhat more effective regenerant than methanol, and both are substantially more effective than the other solvents.

Solvent Regeneration of Non-Functionalized Polymers

Macroreticular styrene-divinylbenzene adsorbents are generally known to be more easily regenerated by solvents than are carbons. This was confirmed for fixed-bed regeneration of Amberlite XAD-4[8] and Polysciences 100% poly(divinylbenzene), as shown in Table II.

Solvent Regeneration of Basic Polymeric Sorbents

Fixed-bed regenerations of several basic sorbents are also reported in Table II. Reilly Tar & Chemical poly(4-vinyl pyridine) [PVP] showed full and efficient regenerability with methanol, acetone and methyl acetate. The result shown for Dowex WGR (tertiary amine) resin is for regeneration with dimethyl sulfoxide (DMSO), for which regeneration is both slow and incomplete. Other runs with Dowex WGR[8] used methanol regenerant with a smaller and less efficient bed volume, and showed slow and incomplete regeneration, comparable to the result with DMSO.

Batch equilibration experiments were also carried out with Dowex WGR. In experiments where the resin was loaded to equilibrium with 8% aqueous acetic acid solution (w/w) and contacted with 5 g of solvent per g of wet resin, recoveries of acetic acid with methanol and DMSO were 27% and 34%, respectively. Tertiary amines in solvent mixtures with chloroform or various ketones have been found to be effective liquid extractants for recovering acetic acid from water[9,10]. These mixtures were found to give at most 40% recovery of acetic acid from Dowex WGR in batch equilibrations.

These results and those reported in Table II are consistent with those obtained by Kawabata, et al.[11] for regeneration of amine, poly(vinylpyridine), and styrene-divinylbenzene resins which had taken up adipic acid from aqueous solution. For the tertiary amine resins Kawabata, et al found slow and incomplete regeneration. This difficult regeneration is probably related to the very high basicity of the amine resins, which makes the complex, or ion pair, with acetic acid very difficult to reverse.

Resins with secondary amine groups should be even stronger bases than tertiary amines and still more difficult to regenerate. Polyethyleneimine resin (Table V of Part I) was loaded to 0.51 g acetic acid/g dry polymer and was then contacted with a large excess of methanol (50 mL per g dry polymer), giving a recovery of only 43% of the acetic acid. Duolite A-340 was equilibrated with 6% (w/w) acetic acid solution and then contacted batchwise with 5 g methanol or acetone per g wet resin. Recoveries of acetic acid were 23% and 21% for methanol and acetone, respectively.

The regenerability of Bio-Rad AG-2X8, a quaternary ammonium resin, by solvents was found to be comparable to that of Dowex WGR. AG-2X8, loaded with 0.18 g acetic acid/g dry resin, was contacted with 10 mL ethanol per g dry resin, yielding 30% recovery of acetic acid. The recovery of lactic acid (a stronger acid) loaded onto the resin at 0.23 g/g dry resin, was only 10% under the same conditions. These low removals are in line with the results for removal of adipic acid by fixed-bed regeneration of a hydroxide-form quaternary ammonium resin reported by Kawabata, et al[11].

Since the poly(4-vinylpyridine) resin was much more readily regenerable (Table II) than the amine resins, solvent-regeneration experiments were conducted with Celanese polybenzimidazole (PBI), another weaker base than the amines. When loaded with 0.15 g acetic acid/g dry resin, PBI at 10 mL solvent per g dry resin gave 57% and 46% recovery of acetic acid with methanol and ethanol, respectively. Recovery of lactic acid loaded at 0.17 g/g dry resin was 40% with ethanol.

Amberlite XAD-12 affords yet another kind of basic group (N oxide). Samples of XAD-12 were equilibrated with 6% (w/w) aqueous acetic acid solution giving a loading of 0.30 g acetic acid/g dry resin, and were then contacted with 5 g solvent/g wet resin. Recoveries of acetic acid were 41% and 48% with methanol and acetone, respectively.

In order to compare regeneration by vaporization with regeneration by solvent leaching, Dowex WGR, Dowex MWA-1, and Bio-Rad AG-2X8 were each equilibrated with 5% (w/w) aqueous acetic acid solution, centrifuged, and allowed to dry at 66°C under 25 mm Hg vacuum until a constant weight was reached. Removals of acetic acid were determined by weight difference and elemental analysis for nitrogen, and were 100%, 45%, and 75% for MWA-1, WGR, and AG-2X8, respectively. Both WGR and AG-2X8 gave evidence of thermal decomposition under these conditions. Dowex MWA-1 is stated by the manufacturer to be stable up to 100°C, and was found to have the same capacity for acetic acid after regeneration by heating, when contacted with aqueous acetic acid solution again. It may be possible to regenerate Dowex MWA-1 satisfactorily at an elevated temperature, still below 100°C.

CONCLUSION

Activated carbons which have taken up acetic acid and water from aqueous solution are in general readily regenerable by methanol and methyl acetate, and, somewhat less efficiently, by acetone. Amoco GX-031 is an exception, showing incomplete regeneration.

Macroreticular styrene-divinylbenzene adsorbents have substantiallly lower capacities (Part II) and poorer selectivities than the carbon adsorbents, but are regenerated fully and somewhat more efficiently by methanol.

Among basic polymeric resins, the various amines (Dowex WGR, Duolite A-340, PEI, and Bio-Rad AG-2X8) were not fully regenerable by solvent leaching, nor was Amberlite XAD-12, a poly N-oxide. It may be possible to regenerate Dowex MWA-1, a tertiary amine resin, at higher temperatures.

Polybenzimidazole, a weaker base, gave higher recoveries of acetic acid in batch experiments than did the amines and the N oxide. Poly(4-vinyl pyridine) gave good regeneration properties in fixed-bed experiments with methanol, methyl acetate, and acetone, but has a large water uptake with substantial swelling when contacted with aqueous acetic acid solutions (Part II). Additional cross-linking of that polymer may reduce swelling.

The results with basic polymers indicate that one would want an intermediate degree of basicity in a regenerable sorbent for acetic acid, so as to provide acid-base interactions for uptake of acetic acid, while still being regenerable.

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