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RECOVERY OF GRAPEFRUIT OIL FROM PROCESSING WASTE WATER USING SDVB RESINS

A. P. ERICSON, R. F. MATTHEWS, A. A. TEIXERIA AND H. A. MOYE
University of Florida, IFAS
Food Science and Human Nutrition Dept.
Gaineville, Florida 32611

Abstract. **Styrene-divinylbenzene (SDVB) resins were utilized for the recovery of cold-pressed grapefruit oil from model solutions and waste waters. Sorption rates and sorption capacities were determined for a series of resins with model solutions. Citrus oil processing waste water was passed through an upflow column extraction system. Adsorbed oil was desorbed using 95% ethanol and gas chromatographic analysis was performed to determine the quality of the extracted oil. The waste water samples contained suspended solids which reduced the extraction ability of the resins. Major compounds recovered from waste waters were d-limonene and alpha-terpineol. Nootkatone and linalool recovery levels varied, while octanal and decanal were present in extremely low levels.**

The aqueous effluent from the citrus oil extraction and recovery process can contain high levels of the oils (8, 11) which exhibit antimicrobial activity (6), decreasing the effective disposal of effluents through sewage treatment systems dependent on microbial degradation (9). Current methods of treatment involve distillation of volatiles from waste and ultimate recovery in the form of d-limonene (10). Additional recovery of cold-pressed citrus oils would provide increased industry returns, as well as reducing disposal problems (8).

Styrene-divinylbenzene (SDVB) resins can be used to remove organic compounds from industrial waste waters. The resins are durable non-polar polymers that can be easily regenerated with possible recovery of the solutes (4). Recent uses with importance to the food industry include debitterment of grapefruit juice (5) and concentration of orange volatiles (1), apple volatiles (3) and tomato volatiles (7) from aqueous solutions. From this evidence it would seem feasible to use SDVB resins for the recovery of citrus oils from processing waste waters. This study was conducted to test this theory and to develop a process for such an operation.

Materials and Methods

Six commercially available SDVB resins and one Teflon resin were evaluated for their sorption rates and capacities for cold-pressed grapefruit oil from model solutions. The resins and some of their physical properties are listed in Table 1. Using the analysis of centrifuge effluent discharge reported by Parish et al. (8), model solutions were prepared containing a 1.49% sucrose, 0.70% glucose, 0.41% fructose, 0.072% citric acid, and a measured amount of cold-pressed grapefruit oil. The oil was emulsified into the sugar-acid solution by mixing with a Waring blender. Comparative rates of adsorption were determined by setting up batch systems for each resin and exposing 1.0 g of resin to 50 mL of model solution for time periods of 5 min to 4 hr. After each treatment, the model solution was separated from the adsorbent and analyzed for recoverable oil. The fractional concentration of oil remaining in solution was plotted against time on semi-log plots, and linear regressions were obtained. The steepness of the slopes was indicative of the sorption rates.

Sorption capacities were determined by mixing 50 mL of model solution at various oil concentrations with different weights of resin for 24 hr periods in screw top test tubes. The equilibrium oil concentration in solution was determined and the mass of oil adsorbed was calculated by the difference between the concentrations of adsorbate in solution measured for controls and the resin samples. Freundlich isotherms were obtained by plotting the adsorptive capacity calculated as mg oil/g resin against the equilibrium solution concentration expressed as mg oil/ml solution on log-log coordinates.

The resin with the fastest sorption rate and highest sorption capacity was selected for use in a column system to extract oil from model solutions. A glass column (11 mm x 30 cm) was packed with 10 mL of the best performing resin (measured dry) which was soaked overnight in 95% ethanol. After rinsing the sorbent bed with 5 to 10 bed volumes (BV) of water, model solution was pumped downflow through the column at 33 BV/hr. The influent and effluent oil concentrations were monitored and operation was stopped when the effluent concentration was equal to the influent concentration. Breakthrough curves were plotted. The extracted oil was desorbed with 4 to 5 BV of 95% ethanol.

Several samples of citrus oil processing waste water streams were obtained from Florida citrus plants. Using the best performing resin from above, sorption rates and capacities for the resin in waste water samples were determined and compared to that found with model solutions. In separate experiments, oil was extracted from waste water samples using column and batch processes. One downflow column experiment was attempted as described

Table 1. Physical properties of Styrene-divinybenzene resins.

Resin	Cross-linking (% DVB)	Porosity (%)	Pore Diameter (Angstroms)	Surface Area (m^2/g)	Bulk Density (g/cc)[w]
XFS-4257[z]	50	35	100	450	0.444
XFS-4022[z]	20	35	200	80-120	0.419
XUS-40323[z]	65	27	25	550	0.411
XUS-40322[z]	65	46	50	650	0.267
XAD-16[y]	—	66	144	860	0.266
XAD-4[y]	—	54	65	768	0.496
Teflon[x]	—	—	—	—	0.762

[z]Dow Chemical
[y]Rohm and Haas
[x]Dupont Chemical (resin made of polytetrafluoroethylene)
[w]Bulk densities determined, all other values reported by manufacturer. All particle sizes reported as 20-50 mesh.

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above. An upflow fluidized-bed column system was also attempted. In this sytem, the sample entered the column at the bottom and effluent exited at the top. Flow rate (15 BV/hr) was adjusted to suspend the resin beads in fluidized motion without forcing them out the top of the column. A screen-equipped adapter was placed at the top of the column to assure that resin would not escape.

One batch experiment using 10 mL (2.52 g) of dry resin was combined with 500 mL of citrus oil processing waste water in a 1 L Erlenmeyer flask. The mixture was agitated on a stir-plate at room temperature for 3 hr. At the end of the 3 hr treatment time the mixture was transferred to a 1 L separatory funnel where the resin was separated from the waste water by flotation. After separating and rinsing with some water, the resin was flushed from the separatory funnel with 95% ethanol into a glass column and the adsorbed oil was subsequently desorbed by downflow with 95% ethanol as above.

The recoverable oil of all solutions in the study was determined by the Scott method adapted by Carter (2). The components of the grapefruit oil control and all extracts were analyzed by capillary gas chromatography using a Perkin Elmer Sigma 3B chromatograph connected to a Spectra-Physics SP4400 ChromJet integrator. Chromatographic parameters were as follows: DB-5 capillary column (30 m x 0.32 mm ID), injection volume was 2 uL and split ratio 1:57, injection port at 200°C, flame ionization detector at 325°C, temperature program: 2 min, 55°C; 3.5 °C/min to 250°C for 10 min, helium carrier gas at constant back pressure of 9.5 psig.

The regression lines of the sorption rate and isotherm data were compared by conducting analysis of variance (based on t-values) on the slopes and intercepts using the Statistical Analysis System (SAS). In all statistical tests, the differences were considered significant at the 5% level (p-value < 0.05).

Results and Discussion

Resins XUS-40322 and XUS-40323 (Dow Chemical) and resins XAD-4 and XAD-16 (Rohm and Haas) were found to have similar rapid sorption rates. The resin XUS-40323 had the highest sorption capacity (2.1 g/g) determined with Freundlich isotherms and was used in additional experiments.

In downflow fixed-bed column experiments using model solutions, rapid flow rates (33 BV/hr) could be used with less than 10% leakage of oil. The effluent concentration curves (Fig. 1) display typical characteristics of column operations described by Treybal (12). The capacity of the resin in the column system was 2.0 g/g, which is similar to that found from its Freundlich isotherm. No apparent chemical changes of the oil components were found when analyzing the extracts by gas chromatography.

Citrus oil processing waste water samples contained suspended solids which greatly interfered with the extraction procedure. Since most of the oil was found to be associated with the suspended solids, removal of the solids prior to extraction was not practical. The sorption capacity of the resin in the waste water was 0.5 g/g (Freundlich isotherm determination), which is approximately 25% of that in the model solution. This is thought to be due to the competing surface area available for adsorption provided by the suspended solids.

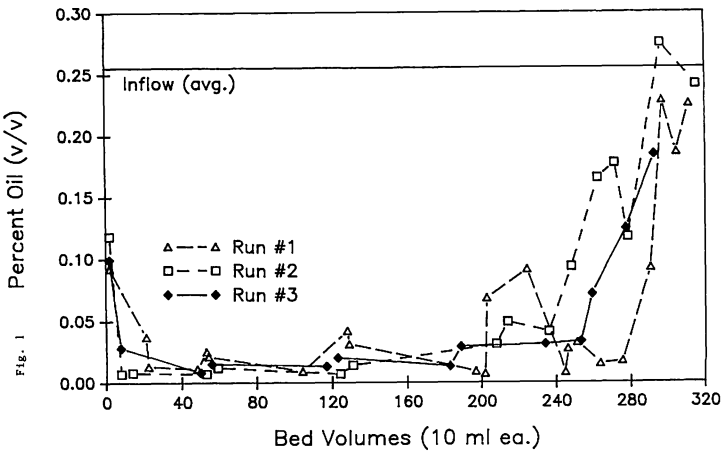

Fig. 1. Downflow fixed-bed column effluent curves for resin XUS-40323 with model solutions.

Downflow fixed-bed column operation with the waste water samples was ineffective because the suspended solids restricted flow through the column. Upflow fluidized-bed column operations resulted in recoveries up to 74% for the oil present in the stream. However, part of the recovery was due to the collection of suspended solids by a screen at the column exit forming a filter cake. Flow became restricted before resin saturation occurred. The effluent concentration curves (Fig. 2) displayed variable levels of leakage and no distinct breakthrough points were evident. In order to desorb the oil, mechanical agitation of the cake and resin was required.

Due to the problems encountered with column operations, a batch system was conducted and resulted in an oil recovery of 67.2%. Resin beads were easily separated from the suspended solids of the waste water and, as a result, desorption could be carried out with less difficulty. Higher recoveries could be obtained with a batch system by using multiple treatment stages.

A comparison of chromatograms for grapefruit oil extracted from the model solution and an extract from processing waste water is displayed in Figure 3. The most pronounced difference is the much higher concentration of alpha-terpineol and the near absences of octanal and decanal in the waste water extract. This was observed in all

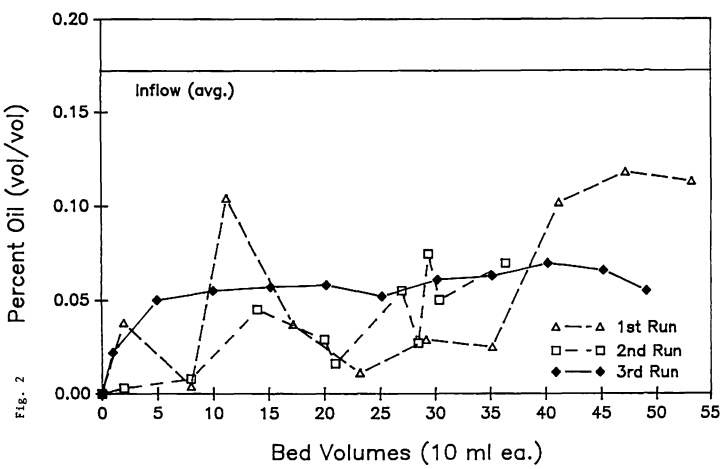

Fig. 2. Upflow fluidized-bed column effluent curves for resin XUS-40323 with waste water.

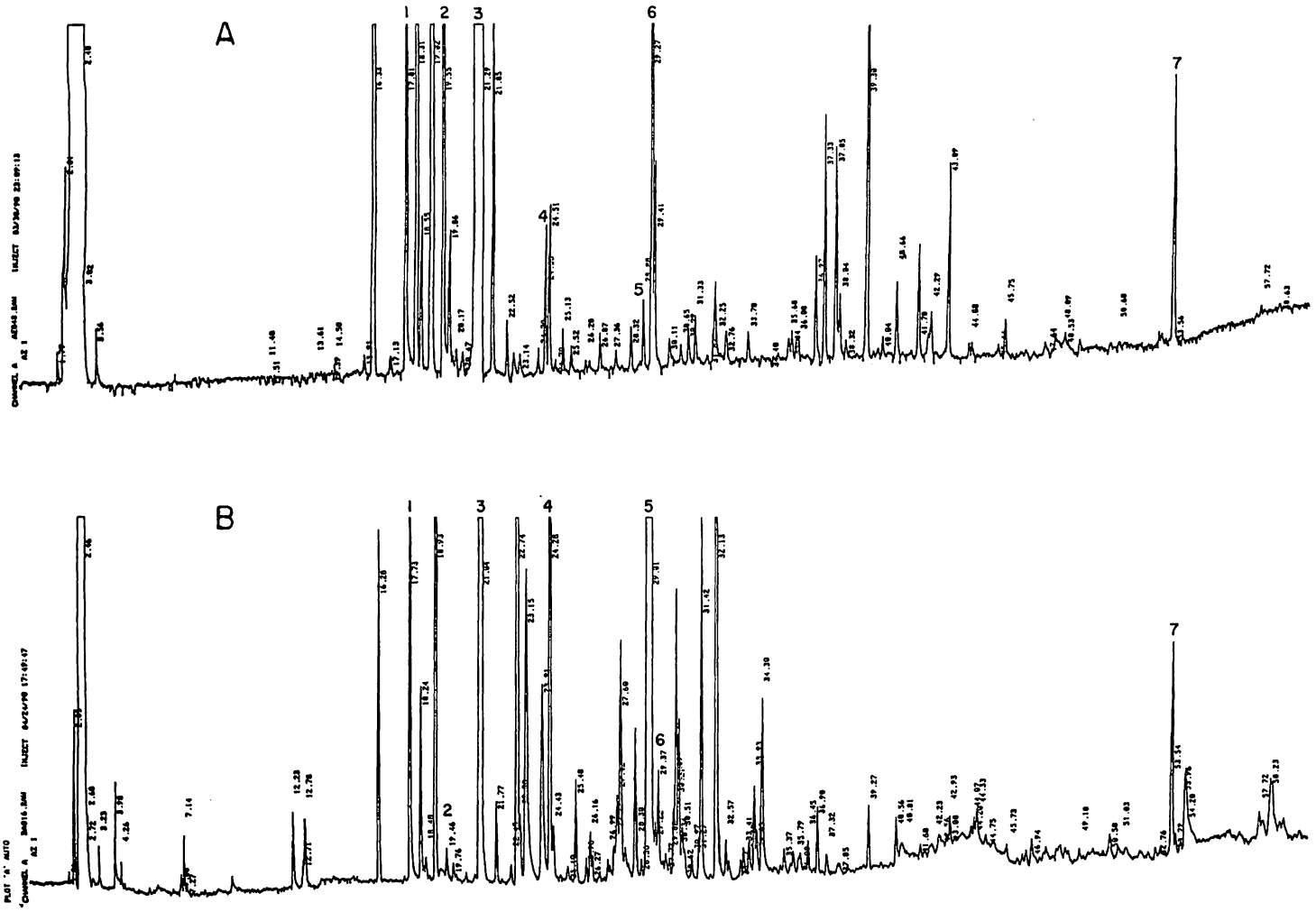

Fig. 3. Chromatograms; (A) grapefruit oil extracted from model solution, (B) extract from processing waste water. Labeled peaks are; (1) 1-heptanol (internal standard), (2) octanal, (3) limonene, (4) linalool, (5) alpha-terpineol, (6) decanal, (7) nootkatone.

Table 2. Concentration ratios of selected components of grapefruit oil control and combined fractions of waste water sample extracts.

Compound	Control	Run #1	Run #2
Octanal	0.0114	0.0001	0.0008
Limonene	0.972	0.609	0.648
Linalool	0.0012	0.0034	0.0028
alpha-Terpineol	0.0009	0.381	0.342
Decanal	0.0060	0.0008	0.0002
Nootkatone	0.0024	0.0013	0.0021

the waste water extracts analyzed by gas chromatography. Linalool levels were higher while nootkatone levels in the extracts varied. The relative concentrations of the solute components are listed in Table 2. The extraction process could result in increased recoveries of d-limonene, alpha-terpineol and nootkatone. Reduced waste treatment problems associated with the oil content of oil-mill effluents is an additional benefit.

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