

Liquid – liquid extraction of phenol from simulated sebacic acid wastewater

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Phenol was extracted from sebacic acid wastewater (SAWW) using liquid-liquid extraction in batch as well as serial modes by applying different solvent: SAWW (1:250 - 5:250, v/v). Alcohols (1-hexanol, 1-heptanol, and 1-octanol), castor oil and Aliquat-336® were used for phenol extraction. In a typical extraction experiment involving shaking and allowing for phase separation, phenol (75-96%) can be extracted with different solvents using solvent-wastewater ratio (5:250 v/v). Generally, extraction (%) increased with solvent ratio; however, chain length of alcohols did not affect extractability of phenol much. Best extraction of phenol occurred into Aliquat 336.

Keywords: Ion-pair, Liquid-liquid extraction, Phenol, Sebacic acid wastewater (SAWW)

Introduction

Phenol is a major pollutant present in wastewaters from several industrial activities (coal mining and gasification, petroleum refining, pharmaceutical production, steel and iron manufacture, tanning and finishing of leather and sebacic acid manufacture). In India, desirable limit for phenol^{1,2} is: drinking water, 0.001; effluents for inland surface water, 1; and sewer discharge, 5 mg/l. Phenol in higher concentration is toxic to fish and imparts objectionable taste to water. Methods for remediation of phenol containing effluents include biological^{3,4}, adsorption on activated carbon⁵ and liquid phase chemical oxidation^{4,6-9}. Fenton oxidation, electro- and photo- catalytic oxidations¹⁰, catalytic wet air oxidation¹¹⁻¹³, super critical oxidation¹⁴, membrane techniques¹⁵, emulsion membrane treatment¹⁶, and liquid-liquid extraction¹⁷ are recently developed methods. Biological treatment, although economical, cannot be successful for streams that contain high phenol load¹⁷⁻¹⁹. Bevilaqua *et al*²⁰ addressed efficiency of enzymatic treatment using tyrosinase in phenol removal. One of the most widely used methods of phenol removal from concentrated waste streams is solvent extraction using polar organic solvents²¹⁻²³.

Manufacturing of sebacic acid generates²⁴ highly saline liquid effluent containing phenol (2500-3000 mg/l). NEERI presented treatment scheme for sebacic acid wastewater (SAWW), when there was no functional sebacic acid manufacturing unit in India, hence simulated wastewater was chosen. This paper presents liquid-liquid extraction of phenol from SAWW using alcohols (1-hexanol, 1-heptanol, and 1-octanol), castor oil, and Aliquat-336 (A-336).

Experimental

Chemicals

1-Hexanol and 1-heptanol were 99.0% pure (S.D. Fine Chem Ltd, Mumbai). 1-Octanol (98%) and tricaprlyl methyl ammonium chloride [$R_3N^+(CH_3)Cl^-$, R = $-CH_2(CH_2)_6-CH_3$; A-336] were procured from Sisco Res Lab, Pvt Ltd, Mumbai. Castor oil was purchased from Raj Chemicals, Nagpur. AR grade sodium chloride, and GR grade hydrogen chloride (35% HCl) were purchased from E. Merck (India) Pvt Ltd, Mumbai. Commercial grade sodium sulfate and sebacic acid were used. Phenol (AR) was procured from S.D. Fine Chem Ltd, Mumbai.

Preparation and Characteristics of Simulated Wastewater

Wastewater was prepared in laboratory as per typical composition²⁴ by mixing in tap water requisite quantities of: sebacic acid, 3.0; phenol, 2.5; and sodium sulphate, 80.0 g. Simulated wastewater has: pH, 5.0; average TDS conc., 82400 mg/l; and COD, 8600-8846 mg/l.

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Table 1—Batch and serial extraction of phenol from sebacic acid wastewater (SAWW) by hexanol, heptanol, octanol, castor oil and Aliquat 336

Solv./S No.	Phenol mg/l	% E	Phenol mg/l	% E	Phenol mg/l	% E	Phenol mg/l	% E	Phenol mg/l	% E
<i>Hexanol</i>	<i>1 ml</i>		<i>2 ml</i>		<i>3 ml</i>		<i>4 ml</i>		<i>5 ml</i>	
SAWW	2500		2500		2500		2500		2500	
I	1630	34.8	1630	41.6	1367	45.3	1289	48.4	1087	56.5
II	1459	41.6	1289	48.4	1040	58.4	854	65.8	730	70.8
III	1367	45.3	1040	58.4	839	66.5	621	75.2	512	79.5
IV	1289	48.4	854	65.8	621	75.2	512	79.5	419	83.3
V	1086	56.5	730	70.8	512	79.5	450	82.0	342	86.3
<i>Heptanol</i>	<i>1 ml</i>		<i>2 ml</i>		<i>3 ml</i>		<i>4 ml</i>		<i>5 ml</i>	
SAWW	2500		2500		2500		2500		2500	
I	1708	31.7	1600	36.0	1428	42.8	1250	50.3	1125	55.3
II	1600	36.0	1250	49.7	1071	57.1	925	63.4	725	70.8
III	1375	45.3	1000	59.6	870	65.2	700	72.0	625	74.5
IV	1125	55.3	950	62.1	699	70.0	550	78.3	500	80.1
V	1000	60.2	750	70.2	637	74.5	500	80.7	375	84.5
<i>Octanol</i>	<i>1 ml</i>		<i>2 ml</i>		<i>3 ml</i>		<i>4 ml</i>		<i>5 ml</i>	
SAWW	2500		2500		2500		2500		2500	
I	2143	14.3	1887	24.5	1631	34.8	1522	39.1	1304	47.8
II	1941	22.4	1522	39.1	1289	48.4	978	60.9	914	63.4
III	1600	36.0	1227	50.8	994	60.2	792	68.3	652	73.9
IV	1429	42.8	994	60.2	761	69.6	606	75.8	512	79.5
V	1265	49.3	947	62.1	683	72.7	543	78.3	419	83.2
<i>Castor oil</i>	<i>1 ml</i>		<i>2 ml</i>		<i>3 ml</i>		<i>4 ml</i>		<i>5 ml</i>	
SAWW	2500		2500		2500		2500		2500	
I	2127	14.9	1957	21.7	1739	30.4	1550	38.0	1429	42.8
II	1972	21.1	1759	29.8	1522	39.1	1227	50.9	1009	59.6
III	1832	26.7	1382	44.7	1149	54.0	916	63.4	823	67.1
IV	1630	34.8	1258	49.7	1009	59.6	792	68.3	668	73.2
V	1506	39.7	1040	58.4	901	64.0	699	72.0	606	75.8
<i>A-336</i>	<i>1 ml</i>		<i>2 ml</i>		<i>3 ml</i>		<i>4 ml</i>		<i>5 ml</i>	
SAWW	2500		2500		2500		2500		2500	
I	1087	56.5	916	63.4	839	66.5	543	78.3	450	82.0
II	1021	59.2	745	70.2	481	80.7	497	80.1	404	83.9
III	839	66.5	497	80.1	233	90.7	202	91.9	357	85.7
IV	590	76.4	435	82.6	186	92.5	186	92.5	186	92.5
V	450	82.0	404	83.9	124	95.0	155	93.8	93	96.3

Liquid–Liquid Extraction of Phenol

Under newly developed batch and serial extraction method for extraction of phenol from simulated SAWW, for batch mode of experiments, a fixed volume (250 ml) of SAWW was taken into a separating funnel and added a fixed volume of chosen solvent [solvent: SAWW, 1:250 - 5:250 (v/v)]. Mixture was briefly shaken for 20 min and kept aside for 20 min, after which aqueous phase and organic phase got separated. Aqueous phase was collected and residual phenol was measured on a UV-

vis spectrophotometer (Shimadzu, 1650 PC) at 270 nm. Reduction in phenol concentration was deduced as

$$\text{Phenol extraction (\% E)} = 100(C_i - C_f)/C_i$$

where, C_i is initial phenol concentration in aqueous phase and C_f is phenol concentration after solvent extraction.

In serial extraction, same procedure as for batch operation, was repeated by adding a fixed volume solvent again to raffinate (phenol depleted aqueous solution) from

stage I extraction. This procedure was repeated over 5 stages and yielded excellent extraction of phenol into chosen organic solvents. These experiments were also carried out with 2 ml, 3 ml, 4 ml, and 5 ml doses of solvents following serial extraction method with a fixed volume of SAWW (250 ml). Samples were analyzed for residual phenol at each stage. All data were averaged over at least two batches of extraction experiments; batch-to-batch error was 3-5%. All extraction experiments were performed at room temperature ($30 \pm 2^\circ\text{C}$).

Regeneration of Organic Solvent (Extract)

It is imperative to regenerate organic phase (solvent) so that solvent and solute become reusable. For this purpose, A-336 extract from a batch of 250 ml of SAWW was used. To extract (5 ml) was added 250 ml of 1M HCl or NaCl solution, and shaken well. Aqueous phase was tested for phenol as described previously.

Results and Discussion

Aqueous phenolic solutions exhibit a very strong absorption at 270 nm in UV range. Linear curve ($R^2 = 0.99$) passing through origin ($A_{270\text{nm}} = 0.0164 \times [\text{phenol, mg/l}]$) indicated a molar extinction coefficient of 0.0164 mg^{-1}l , and this relation was used for estimations of phenol.

Solvent Extraction

Batch and serial extraction results of phenol removal from SAWW using alcohols (1-hexanol, 1-heptanol, and 1-octanol), castor oil and A-336 are presented (Table 1).

Extraction of Phenol using 1-Hexanol, 1-Heptanol And 1-Octanol

When solvent to SAWW volume is changed from 1:250 to 5:250, batch extraction of phenol for different alcohols changed as: 1-hexanol, 34.8-56.5; 1-heptanol, 31.7-55.3; and 1-octanol 14.3-47.8 % E. Thus, 1-octanol showed lesser extraction efficiency. During serial extraction using hexanol-SAWW (1:250 v/v), % E increased from 34.8 at stage I to 56.5 in stage V. At stage V, %E increased from 56.5 to 86.3, as hexanol-SAWW ratio is increased from 1:250 to 5:250, whereas using solvent-SAWW ratio 5:250, 1-hexanol, 1-heptanol and 1-octanol afforded 86.3, 84.5 and 83.2% E, respectively. A general trend of decrease in phenol extraction (%) has been observed with increasing molecular mass (1-hexanol, 102.17; 1-heptanol, 116.20; and 1-octanol, 130.23 g/mol).

Table 2—Serial extraction of phenol from sebacic acid wastewater (SAWW) as a function of volume ratio of 1-octanol /A-336 and

A-336/1-octanol			
Solv./S No.	Octanol/A-336	Phenol, mg/l	%E
<i>Volume ratio of octanol to A-336</i>			
SAWW		2500	
I	5:1	700	72.0
II	5:2	725	71.0
III	5:3	500	68.0
IV	5:4	325	87.0
V	5:5	190	92.4
<i>Volume ratio of A-336 to octanol</i>			
SAWW		2500	
I	5:1	325	87.0
II	5:2	325	87.0
III	5:3	275	89.0
IV	5:4	350	86.0
V	5:5	350	86.0

Extraction of Phenol using Castor Oil

Using castor oil (Table 1), phenol (39.7%) is extracted using 1 ml serial extraction in five cycles. Similarly, phenol (76%) is extracted in 5 cycles using 5 ml serial extraction. At each stage, significant increase in percent extraction appeared. Ricinoleic acid in castor oil has a hydroxyl functional group at twelfth carbon, which causes ricinoleic acid (and castor oil) to be unusually polar, and allows chemical derivatization that is not practical with other vegetable oils.

Extraction of Phenol using Aliquat – 336

A-336, a mixture of C_8 (octyl) and C_{10} (capryl) chains with C_8 predominating, is a quaternary ammonium salt used as a phase transfer catalyst and metal extraction reagent. Phenol extraction from SAWW, using A-336 (1-5 ml) in first stage of extraction (Table 1), was 56.5, 63.4, 66.5, 78.3, and 82.0 % using 1, 2, 3, 4 and 5 ml for batch extraction. During serial extraction, these values for V-stage extraction were 82.0, 83.9, 93.8, 95.0 and 96.3 %, respectively. Aliquat® 336 showed higher % E compared to castor oil and other alcohols.

Extraction of Phenol using Octanol – Aliquat-336 Mixtures

When volume of 1-octanol was fixed (5 ml) and that of A-336 was varied (1-5 ml), % E gradually increased

from 72.0% to 92.4% (Table 2). In contrast, changing 1-octanol volume (1-5 ml) at a fixed volume of A-336 resulted in maximum phenol extraction (89%). It is inferred that in 1-octanol + A-336 mixtures, role of A-336 predominates in extraction process.

Effect of Salt on Phenol Extraction

SAWW contained Na_2SO_4 (8%) and sebacic acid (< 1000 mg/l) along with phenol. To assess whether excess Na_2SO_4 influences extraction of phenol, phenol extraction was carried out using hexanol, heptanol, octanol, and A-336 from aqueous phenol solutions, without salt. Accordingly, phenol solution (2500 mg/l) was prepared for extraction purpose. Only single stage batch extraction using 5 ml of each solvent separately was carried out. Extraction of phenol from aqueous phenol solution was quite low (Table 3) using: 1-octanol, 13.6; heptanol, 20; and hexanol, 21.1%. Use of A-336 resulted in 61.5% extraction. Phenol is better extracted from SAWW when compared to aqueous phenol solution (Table 3). Moreover, phenol is also better extracted from phenol + Na_2SO_4 (8%) aqueous solutions. In this case, salt addition increased phenol extraction from 13.6 to 56.5 %, when 1-octanol was used. Thus ionic strength of aqueous solution or wastewater exerts a definite influence on percent extractability of phenol.

Regeneration of Spent Solvent

Spent A-336, which afforded higher phenol extraction, was regenerated (95-100%) using 1N NaCl.

Table 3—Comparison of batch extraction of phenol from from aq. phenol solution and sebacic acid wastewater (SAWW) by octanol, heptanol, hexanol and A-336

S No.	Solvent 5 ml	Extracted from aq. phenol solution, %	Extracted from SAWW, %
1	Octanol	13.6	47.8
2	Heptanol	19.9	55.3
3	Hexanol	21.1	56.5
4	A-336	61.5	87.0

Similar regeneration efficiencies can be attained using 1N HCl.

Partition Coefficient (PC)

A PC or distribution coefficient, which is a measure of differential solubility of a compound in two solvents, was estimated (based on experimental data in Table 1) as

$$PC = [(C_o - C_f)/C_o] \times V_{aq}/V_{org}$$

where, V_{aq} and V_{org} are volumes of aqueous and organic phases, respectively.

PC (40-70) of phenol in linear alcohol-water systems (Table 4) indicates excellent extractability of phenol into these solvents. Constant values for PC of linear alcohol-water systems suggest that phenol does not undergo any molecular association/dissociation in these solvents. However, partition of phenol into castor oil is somewhat less favored, may be due to higher polarity of ricinoleic acid. Phenol (PCs, 214-330) partitions into A-336 almost quantitatively. Thus, partitioning of phenol into A-336 is 4-5 times higher compared to linear alcohols used. Further, in both castor oil and A-336, PCs showed wider distribution suggesting that in these solvents phenol may undergo dissociative-complexation. Concerning phenol extraction from coal-gasification wastewater using diisopropyl ether, butyl acetate, methylisobutylketone and 30% tributyl phosphate-kerosine, Yang *et al*¹⁷ found PCs as 36.5, 71, 100 and 171.9, respectively. Superior partitioning of phenol is possible at lower solvent-water ratio (1:250 to 5:250) used in present study in contrast to Yang *et al*¹⁷ solvent ratio of 1:1 to 1:10.

Some Molecular Interactions during Solvent Extraction of Phenol

Under phenol extraction from SAWW (Fig. 1), phenol might be extracted in the form of a complex [$\{\text{PhOH}\}_x\text{S}_x$]. In linear alcohols possessing -OH group, solvation through hydrogen bonding between O.....H of solvent-phenol pair or, H.....O of solvent-phenol pair may be

Table 4—Estimated phenol partition coefficients for different solvent-water systems

Volume, ml	1-hexanol	1-heptanol	1-octanol	Castor oil	A-336
1	67.0	70.1	41.8	43.9	329.5
2	66.9	70.3	40.6	34.8	214.0
3	68.7	62.7	44.6	36.2	162.8
4	58.2	62.5	40.8	19.2	222.4
5	64.3	61.1	46.0	37.6	227.8

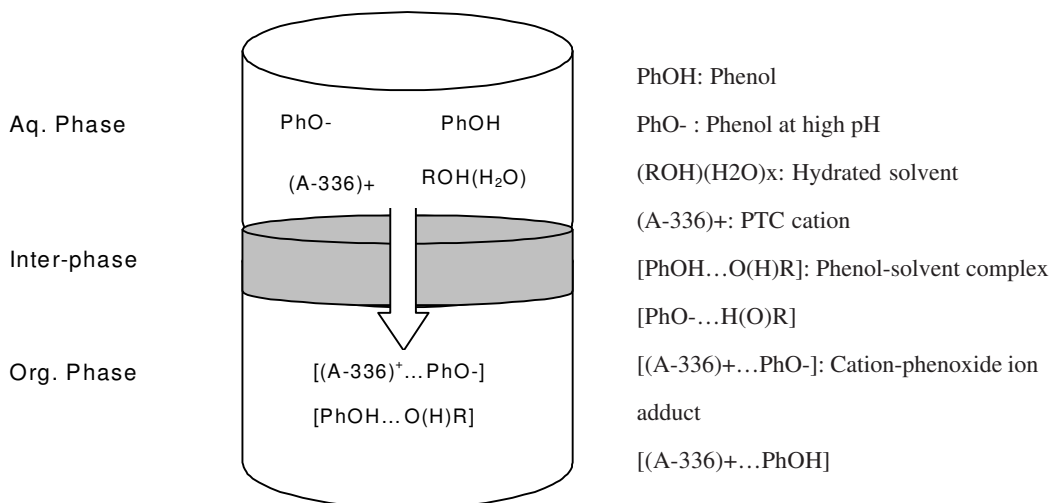


Fig. 1—Solvent-phenol interactions in three phases during solvent extraction of phenol from sebaccic acid wastewater

expected. Hexanol, heptanol and octanol solvents and to some extent castor oil may be expected to extract phenol through hydrogen bond formation. Relative abilities of these solvents may be dependent on strength and number of hydrogen bonds they form with phenol. On other hand, A-336 is a large organic cation with permanent positive charge, and $[(A-336)^+ \dots PhOH]$ or $[(A-336)^+ \dots PhO^-]$ type of interaction may be responsible for higher phenol extraction into this solvent. Inoue & Shishido²⁵ examined distribution equilibriums in solvent extractions of phenol with various mineral acid salts of high molecular weight amines and reported that extraction is greatly enhanced by converting free base amines into their hydrochloric acid salts (A-336).

Conclusions

It is possible to extract phenol (76-96%) from SAWW using C_6 -, C_7 -, C_8 -linear alcohols, castor oil and A-336. Almost quantitative extraction (96%) can be carried out at very low solvent-to-wastewater ratio using A-336 with large PCs. Considering initial phenol concentration of 2500 mg/l, this high percent extraction efficiency would leave out aqueous phase having about 100 mg/l phenol, which may be further treated using established methods. Possibility of regeneration of spent solvent (A-336), by contacting with simple salt solution may imply more stages of reuse of the solvent for extraction. Extraction using A - 336 involves ion-pair formation $[(A-336)^+ PhO^-]$, which is responsible for its higher extraction efficiency and large partition coefficient.

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