

BABLY PRASAD*, GURDEEP SINGH*

REMOVAL OF PHENOLS FROM COKE-PLANT WASTEWATER BY SOLVENT EXTRACTION

Solvent extraction of phenols from coke-plant ammonia liquor has been carried out using four organic solvents, i.e. methyl isobutyl ketone, butyl acetate, di-isopropyl ether and benzene. The extraction efficiency of these solvents has been determined at the original pH (8.5 to 9.0) of coke-oven effluents and at the pH < 7.

The effect of pH on distribution coefficient of phenol for these solvents has been determined in the system composed of pure phenol, organic solvents and buffered water solution.

The percentage efficiency of phenol extraction has been determined in different volume ratio of organic solvent/coke-oven effluents at pH < 7 and temperature of 30°C.

1. INTRODUCTION

Coke is manufactured by high temperature carbonization of bituminous coal. During the coking process, coal gas produced is cooled by considerable amount of water. This generates ammonia liquor, contaminated with organic and inorganic compounds. The conventional contaminants are mainly phenols, ammonia, cyanides, oil and grease and sulphur compounds [1]. All these contaminants, if not removed from wastewater before it is discharged into fresh water stream, will have extremely adverse impact on aquatic life of fresh water stream.

Removal of phenol from coke-oven wastewater is of much concern because of its toxicity. Phenolic compounds can adversely affect fresh water fishes by direct toxicity to fish and fish-food organisms by lowering the amount of available oxygen because of the high oxygen demand of the compounds and by tainting the fish flesh [2]. Various environmental conditions will increase the toxicity of phenol. Lower concentrations of dissolved oxygen, increased salinity and increased temperature all enhance the toxicity of phenol. The phenols are known to create taste and odour problems. Fishes having non-toxic levels of phenol are found to be tainted.

*Centre of Mining Environment, Indian School of Mines, Dhanbad-826004, India.
Correspondence should be sent to G. Singh.

There are mainly two types of the methods for removing contaminants from coke-oven effluents [3]: concentration processes and destruction processes.

In concentration processes, contaminants are recovered as by-products. Solvent extraction is one of the most useful recovery processes of phenols from coke-oven effluents. Organic solvents used in this process should have the following characteristics: high value of distribution coefficient (K) for phenols, boiling point much lower than that of the phenols, low solubility in water, thermal and chemical stability.

High value of K is governed by pH of the water phase. At $\text{pH} > 8$ a significant amount of phenols are in ionized form, thus decreasing the K value. A simple equation for the pH effect upon the distribution coefficient (K) has been given by TRYBAL [4]:

$$K = \frac{K_{\text{low}} \text{pH}}{(Ka/H^+) + 1} \quad (1)$$

where:

K – apparent distribution coefficient for phenols,

Ka – acid dissociation constant,

$K_{\text{low}} \text{pH}$ – distribution coefficient for phenols at low pH (measured experimentally),

H^+ – molar concentration of hydrogen ion.

At low pH values ($\text{pH} < 8$) phenol is practically in the non-ionized form. The concentration of ionized form is lower than 1.05% of the total phenol concentration in the aqueous solution. The Ka/H^+ value in eq. (1) can practically be neglected. In lower pH value ($\text{pH} < 8$) the value of K is independent of pH.

There are many solvents which have been used for solvent extraction of phenols from coke-oven effluents. In earlier days benzene, tricresyl phosphate and butyl acetate (BA) have been used. Presently for removal of phenols, di-isopropyl ether (DIPE) is the most common solvent used [5]. Methyl isobutyl ketone (MIBK) has been reported by SCHEIBEL [6] as a better solvent for phenol recovery.

Basic aims of the present investigation are as follows:

1. To evaluate the efficiency of four organic solvents, namely MIBK, BA, DIPE and benzene for phenol recovery from coke-oven effluents at the original pH ranging from 8.5 to 9.0 and at the $\text{pH} < 7$. (At $\text{pH} < 7$ it is assumed that the ionization of phenol is minimized).

2. To evaluate the effect of pH on K value in the system consisting of pure phenol–organic solvents–buffered water solution.

3. To evaluate the percentage removal of phenols in different volume ratio of organic solvent/wastewater system at $\text{pH} < 7$ and at temperature of 30 °C.

2. METHODOLOGY

The experiments were carried out in 250 cm³ bottles at a constant temperature of 30°C. In each set of experiment, bottles containing the samples were shaken by a shaker for 30 minutes and thereafter transferred into separating funnels for phase separation lasting for 60 minutes. After separation of two phases, phenol concentration in water phase was

determined by phenate method [7] using Shimadzu UV-VIS spectrophotometer. The pH of solutions were measured using Toshniwal digital pH-meter. The value of K was calculated using formula given by KOREMAN [8]:

$$K = \frac{S_o V_w}{(S - S_o) V_o} \quad (2)$$

where:

- K – distribution coefficient,
- S_o – phenol content in organic phase,
- S – initial phenol content,
- V_w – volume of aqueous phase,
- V_o – volume of organic phase.

In the first series of experiments, extraction ability of MIBK, BA, DIPE and benzene were evaluated at the pH of coke-oven effluents ranging from 8.5 to 9.0 and also at the pH = 7. MIBK and DIPE used are of laboratory reagent-grade (98% pure), while benzene and *n*-butyl acetate used are extrapure (99.7%). Coke-oven ammonia liquors were collected from the Lodna and Bhawra coke-plants of Bharat Coking Coal Limited. The pH of ammonia liquor used amounts from 8.5 to 9.0 and phenol concentration ranges from 1500 to 2000 mg/dm³. In the second series of experiments, the effect of pH on distribution coefficient of phenol, between organic solvents mentioned earlier and water solution, was determined. Water solution was prepared from sodium carbonate, buffered distilled water and about 2 g of analytically pure phenol crystals. Small amounts of sulphuric acid and sodium hydroxide were used for pH adjustment. In third series of experiments, different volume ratio of organic solvents/wastewater were taken to determine the percentage efficiency of phenol extraction in one extraction stage. The following formula given by KOREMAN [8] was used for the calculation:

$$\Delta = \frac{S_o \cdot 100}{S} \% \quad (3)$$

where

- Δ – degree of phenol extraction,
- S_o – phenol content in organic phase,
- S – initial phenol concentration.

Percentage efficiency of phenol extraction in three extraction stages have been theoretically calculated.

3. RESULTS AND DISCUSSION

The K values of phenol for different solvents are given in table 1. The results indicate that MIBK displays maximum distribution coefficient for phenols. In fig. 1, the phase equilibrium curves for wastewater–organic solvent system are shown. The decreased value of distribution coefficient at the pH = 8.5 clearly indicates that fraction

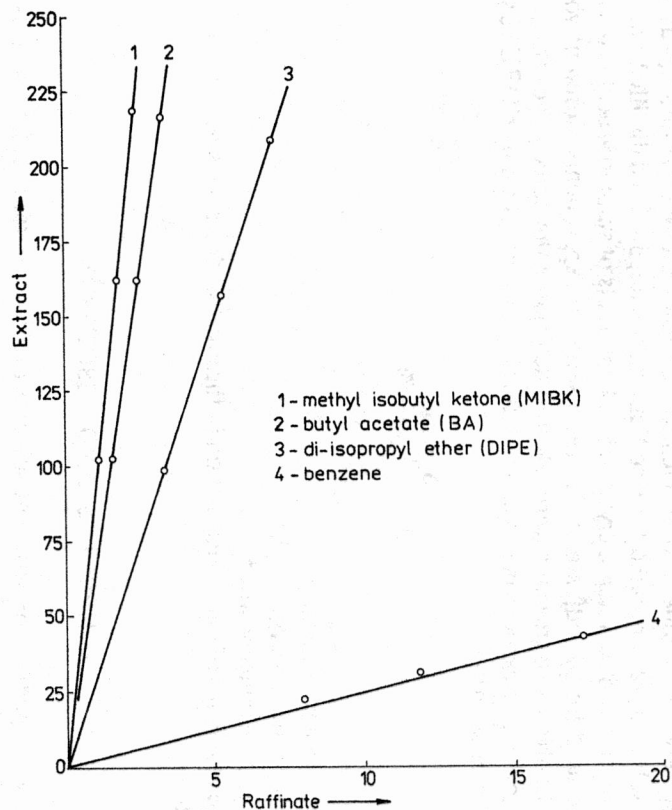


Fig. 1. Phase equilibrium curves for coke-plant wastewater (contaminated with phenol) –organic solvent system. Phenol contents in extract and raffinate are expressed in $\text{mg}/50 \text{ cm}^3$. Measurement conditions: $\text{pH} < 7$, temperature -30°C

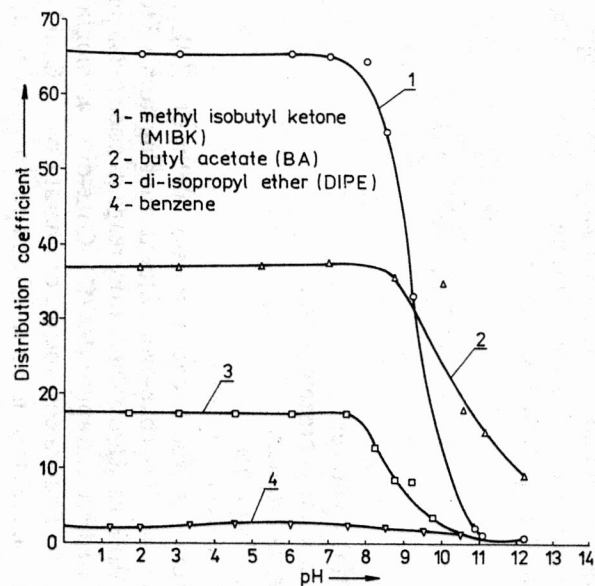


Fig. 2. Distribution coefficient of pure phenol for organic solvent-buffered water system as a function of pH at 30°C

Table 1

Distribution coefficient K of phenol for different organic solvents at various pH of coke-oven effluents

Solvent	Molecular weight	Boiling point (°C)	Density at 20.2 °C (kg/m ³)	Vapour pressure at 20 °C (mm Hg)	K		Solubility of solvent in water at 20 °C (g/dm ³)
					pH=8.5	pH<7	
MIBK	100.2	116–119	801	6	72	98	17
Butyl acetate	116.16	126.3	881	10	55	68	9
DIPE	102.18	68–69	726	130	20	30	12
Benzene	78.12	80.3	876	76	2	3	0.6

Table 2

Percentage efficiencies of phenol extraction at different volume ratios of DIPE and coke-oven wastewater

Wastewater/DIPE volume ratio	Phenol content in coke-oven effluents at pH<7 (mg/50 cm ³)		Efficiency of phenol removal at first extraction stage*	Theoretically calculated efficiency of phenol removal at next two extraction stages (%)
	Raw wastewater	Raffinate		
5	71.5	11.82	83.45	99.54
10	143.0	36.15	74.72	98.38
12.5	143.0	41.25	71.15	97.59
15	214.5	79.05	63.14	94.99

*Total extraction stages: 3.

of phenols is in ionized form. Taking into consideration the four essential properties of solvents for phenol recovery, benzene shows low K value, but it fulfills satisfactorily the remaining three characteristics. The most important characteristic is the high distribution coefficient for phenol and this has been fulfilled satisfactorily by MIBK.

In fig. 2, the points represent the experimentally measured distribution coefficient (K) of pure phenol for organic solvents and buffered water solution as a function of the pH of the raffinate. The value of K for MIBK has been decreased from 98 (for mixed phenols present in high concentration in coke-oven effluents) to 66 (pure phenol in high concentration in water). This value is nearly constant up to pH = 8. At pH > 8, considerable amount of phenols undergo ionization, showing at the same time a sharp decrease in K values. In the case of BA, DIPE and benzene, K values for high concentration of pure phenol in water are 37, 17.5 and 2.0, respectively. All these values are not affected by pH

change up to 8.0, but above pH 8.0 the sharp decrease in K values has the same explanation as in the case of MIBK.

Percentage efficiencies of phenol extraction at different volume ratio of DIPE and coke-oven wastewater have been shown in table 2. At volume ratio of 15, in one extraction stage more than 63% of phenols have been extracted. In the next two extraction stages, about 95% of phenols (theoretically calculated) have been extracted. This indicates that using 15 volume ratio of coke-oven effluents and DIPE in three extraction stages about 95% of phenols may be extracted from coke-oven effluents (at temperature of 30°C and pH = 7). As it has been proved (table 1), for MIBK the value of distribution coefficient (K) of phenols is three times higher than that for DIPE. Thus, by use of the same volume ratio (15) of coke-oven effluents and MIBK, more than 95% of phenols may be extracted from coke-oven effluent in one or two extraction stages. Solvent recovery following the extraction can be achieved in different ways. According to GREMINGER et al. [9] vacuum-steam stripping is a particularly attractive choice for removal of residual MIBK; this reinforces utility of MIBK as a solvent.

4. CONCLUSIONS

The distribution coefficient (K) of phenol has been evaluated in the system of organic solvent-coke-oven effluents at the pH = 8.5 and pH < 7. It has been found that MIBK displays maximum distribution coefficient for phenols. The effect of pH on distribution coefficient of phenol shows that up to pH 8.0, the K value is independent of pH. But at pH 8, the sharp decrease in K value proves that large fraction of phenol undergoes ionization. The percentage efficiency of phenol extraction from coke-oven effluents using DIPE in 15 volume ratio amounts 95% in three extraction stages at temperature of 30°C and pH = 7. A distribution coefficient of phenols for MIBK is three times greater than that for DIPE. So MIBK may be used in 15 volume ratio with coke-oven effluents to extract more than 95% of phenols in less than three extraction stages. Solvent recovery following extraction process may be achieved by vacuum-steam stripping. This reinforces the utility of MIBK as a solvent.

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USUWANIE FENOLI ZE ŚCIEKÓW KOKSOWNICZYCH METODĄ EKSTRAKЦИИ ROZPUSZCZALNIKOWEJ

Przeprowadzono rozpuszczalnikową ekstrakcję fenoli z amoniakalnych ścieków koksowniczych. W procesie wykorzystano cztery rozpuszczalniki organiczne: keton metylowoizobutyloowy, octan butylu, eter izopropylowy i benzen. Wydajność ekstrakcyjna tych rozpuszczalników została określona dla ścieków koksowniczych o pH 8.5-9,0 i pH < 7,0.

Wpływ odczynu cieczy na współczynnik podziału fenolu w przypadku tych rozpuszczalników został określony w systemie złożonym z czystego fenolu, rozpuszczalników organicznych i roztworu buforowego.

Procentową wydajność ekstrakcji fenoli zbadano w zależności od objętościowego stosunku rozpuszczalników do ścieków koksowniczych przy pH < 7 i temperaturze 30°C.

УДАЛЕНИЕ ФЕНОЛЕЙ ИЗ КОКСОВЫХ СОЧНЫХ ВОД МЕТОДОМ ЭКСТРАГИРОВАНИЯ РАСТВОР СТЕЛЯМИ

Проведено экстрагирование растворителями фенолей из аммиачных коксовых сточных вод. В процессе использовали четыре органических растворителя: метилизобутилкетон, бутилацетат, изопропиловый эфир и бензол. Экстракционная эффективность этих растворителей была определена для коксовых сточных вод pH = 8,5-9,0 и pH < 7,0.

Влияние реакции жидкости на коэффициент деления фенола в случае этих растворителей было определено в системе, состоящей из чистого фенола, органических растворителей и буферного раствора.

Процентная эффективность экстрагирования фенолей исследована в зависимости от объемного отношения растворителей к коксовым сточным водам при pH < 7,0 и температуре 30°C.