



Further studies on phenol removal from aqueous solutions by solvent extraction

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Abstract

The removal of phenol from aqueous solutions by solvent extraction has been investigated. Batch experiments were conducted to determine the effect of different solvents (four solvents) on the rate of phenol removal from dilute aqueous solution. The effect of pH, contact time, solvent/feed ratio, shaking time and agitation speed on the removal of phenol by each solvent were investigated. The equilibrium condition was also determined and the rate of extraction was measured as a function of the above. The performance of each solvent is discussed with respect to the operating conditions. The results lead strongly towards the use of methyl iso-butyl keton (MIBK) and di-isopropyl ether (DIPE) as a preferred solvent. Based on the results of the experiments the operating conditions were proposed and 95-98% phenol was removed depending on the type of solvent used.

1 Introduction

Nature contains many fortunes like coal and petroleum. These natural fortunes usually can not be used in their original form, so they undergo certain treatments to improve their properties, for example, petroleum refinery, coke oven plants and phenol resin plants. These processes are the main cause of the wastewater contamination with phenol, where the concentration of phenol ranges from 1000 ppm to 6000 ppm. Phenols are readily biodegraded unless they are at high concentration, which are toxic to the microorganism and cause flesh of fish. Aqueous phenol solutions make an interesting case study for liquid extraction because they represent a common waste disposal problem.

However, there are many methods have been studied for extraction of phenol from aqueous solutions. Among them is the extraction of phenol using sulfuric acid salts of trioctylamine in a supported liquid membrane [1]. Phenol can be removed from wastewater by the electrochemical technique, which was studied

at platinum and DSA anode [2]. Also phenol can be removed by adsorption on anion exchange resins [3]. The oxidation technique was studied by Al-Enezi, et.al. [4]. Now the activation carbon is widely used as an effective adsorbent of phenol [5, 6, 7]. The use of activated carbon as an adsorbent is much expensive, so the trend now is using other inexpensive adsorbents instead of activated carbon.

Among recovery process solvent, extraction is generally preferable over steam stripping for phenol removal, since the phenol water system form an isotropic at 9.2 wt. % phenol. Benzene, butyl acetate have been used as solvents for extraction in the past, but the most common solvent at present is di-isopropyl ether (DIPE), which is used in the phenosolvan process [8]. Another recent process appears to use methyl iso- butyl keton (MIBK) as a solvent [9, 10, 11].

The aim of the present work is to study the effect of different solvents, namely; DIPE, toluene, benzene and MIBK on the rate of phenol removal from dilute aqueous solution by conducting a series of batch extraction tests using shaker apparatus to optimize the design parameters for the full-scale extraction process. The effect of pH, contact time, solvent/feed ratio, agitation time and speed on the removal of phenol by each solvent were investigated. The equilibrium condition was also determined and the rate of extraction was measured as a function of the above. The performance of each solvent is discussed with respect to the operating conditions.

2 Experimental part

The desired quantity of pure solvent is added to the aqueous phenol solution in a 250-ml glass bottle. Then the bottle is put in a shaker, which can be adjusted at the desired values of agitation (stroke/min), temperature and time.

After the desired time is elapsed, the bottle is taken off from the shaker and the solvent is separated from the aqueous raffinate using separatory funnel, in which the sample is rested for 30 min, so that the separation of the two phases is completely achieved. The concentration of the lower layer is determined by using spectrophotometer (UV-1601 Shimadzu).

3 Results and discussion

3.1 Effect of solvent to feed ratio

Generally, increasing the amount of solvent will increase the removal of the solute from its mother liquor. Figures (1, 2, 3, and 4) show the concentrations of the final aqueous solutions against time for the various solvents at different values of solvent to feed ratio (S/F). Figures (1 & 3), when using DIPE and benzene, indicate that: the changing of S/F ratio from 1:1 to 2:1 has a large effect more than obtained by changing the ratio from 2:1 to 3:1. Also, indicate that, S/F ratio have no affect on the equilibrium time, especially at the higher values of S/F.

Figures (2, & 4), when using toluene and MIBK, indicate that: increasing the S/F ratio will improve the extraction process. It is clear that the optimum residence time for each solvent used is within 15 min, after that time, the rate of decreasing phenol concentration in the final solution is almost constant.

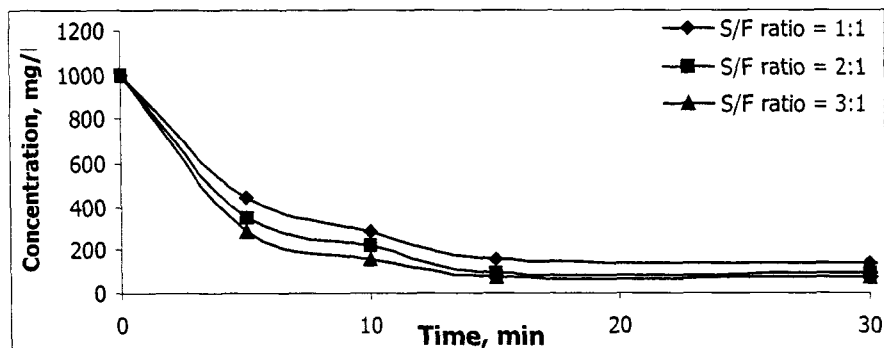


Figure 1: Concentration Vs. time at different solvent to feed ratios using DIPE at 30°C & 100 stroke/min

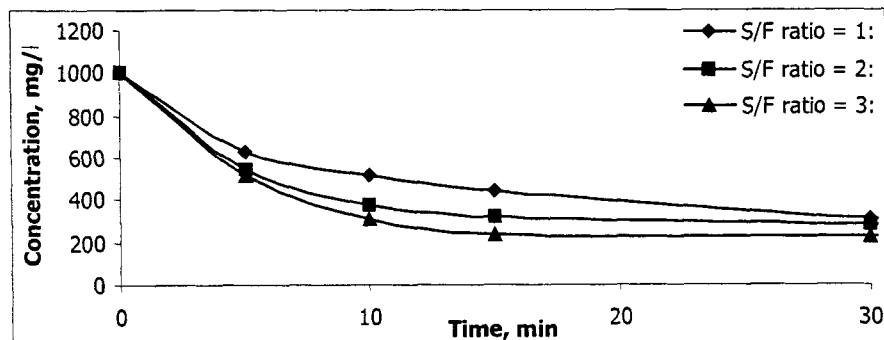


Figure 2: Concentration Vs. time at different solvent to feed ratio using toluene at 30 °C & 100 stroke/min

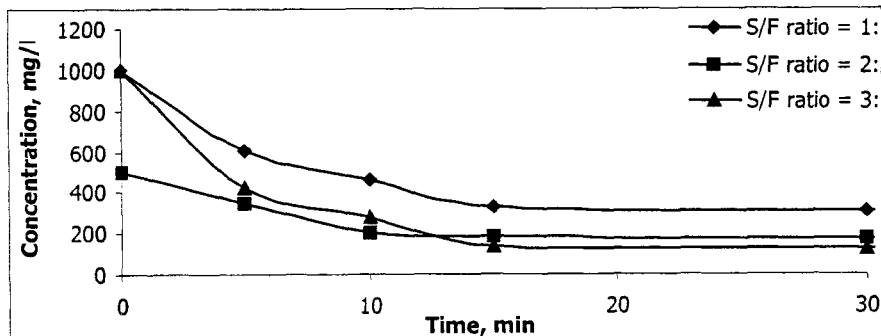
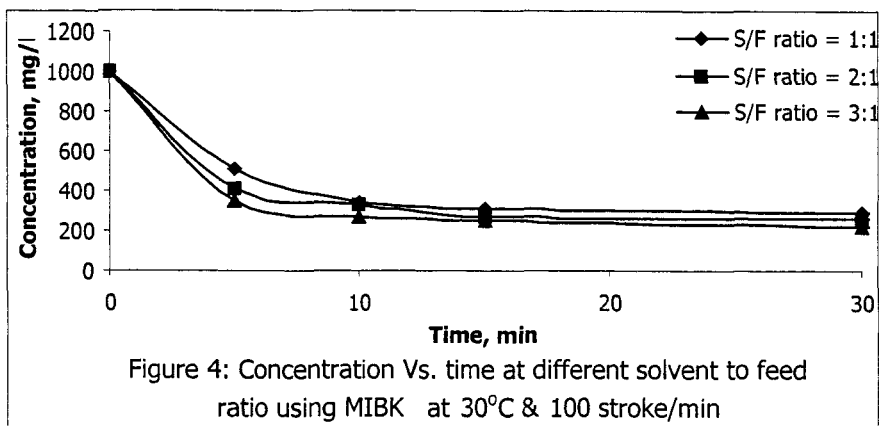


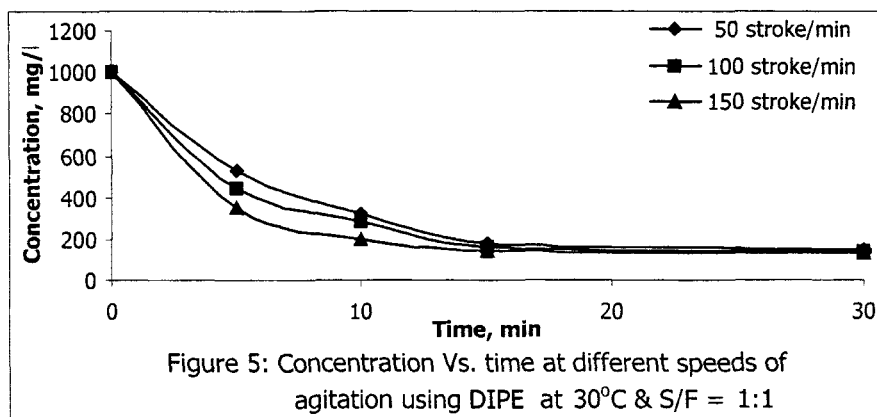
Figure 3: Concentration Vs. time at different solvent to feed ratio using benzene at 30°C & 100 stroke/min



3.2 Effect of agitation speeds

Figures (5, 6, 7, & 8) show the effect of the agitation speed using the different four solvents. These figures indicate that, the extraction rate increases with increasing the agitation speed for all solvents. The extraction process is considered as diffusion controlled in which the contact area increases and hence the rate of mass transfer increases due to the impregnation of one liquid through the other.

Moreover, the figures indicate that, the optimum residence time depends on the solvent used and sometimes on the value of the speed. For example, by using toluene, Figure (6) shows the optimum residence time is about 30 min, after that the decreasing rate of the phenol concentration is nearly constant. While, for the other solvents, the residence time is 15 min. This may be attribute to the low affinity of toluene to extract phenol by varying speed of the process, while the other solvents have high affinity.



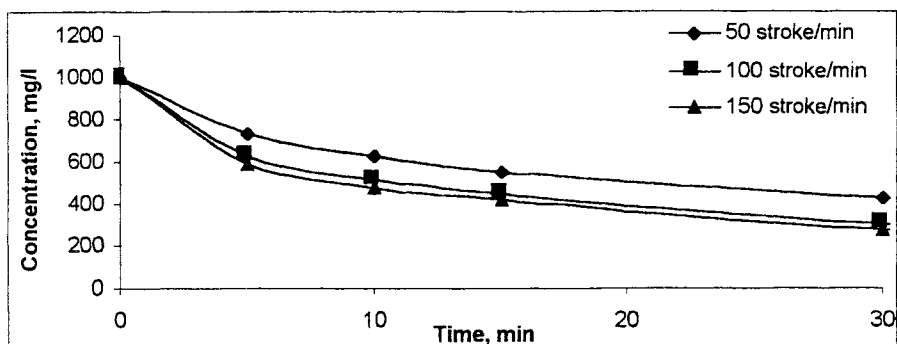


Figure 6: Concentration Vs. time at different speeds of agitation using toluene at 30°C & S/F = 1:1

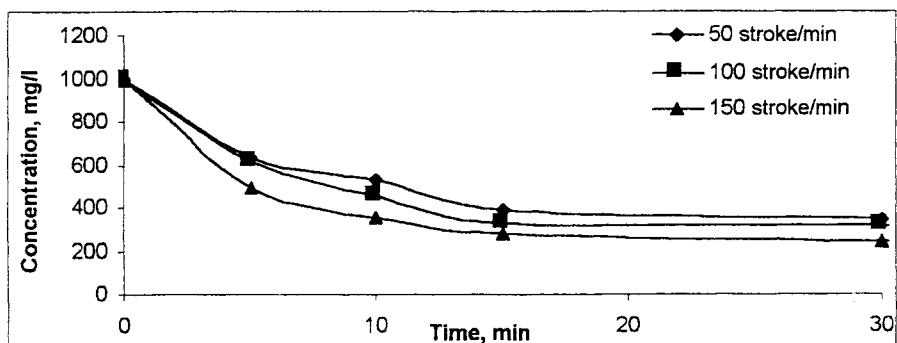


Figure 7: Concentration Vs. time at different speeds of agitation using benzene at 30°C & S/F = 1:1

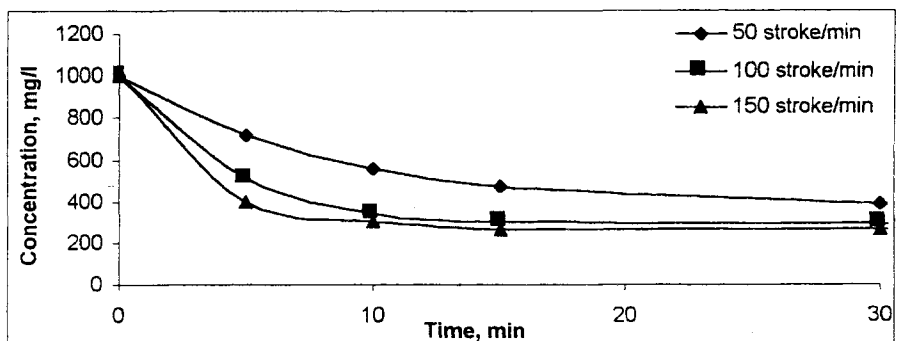


Figure 8: Concentration Vs. time at different speeds of agitation using MIBK at 30°C & S/F = 1:1



3.3 Effect of Temperatures

Figures (9, & 10) show the effects of the temperatures on the rate of phenol removal, by examining these figures, it is noted that, the rate of extraction increases by increasing the temperature. The figures also indicate that, the rate of reaction is slightly increasing with the increasing of the temperatures, which means that the extraction process is physically not chemically in nature.

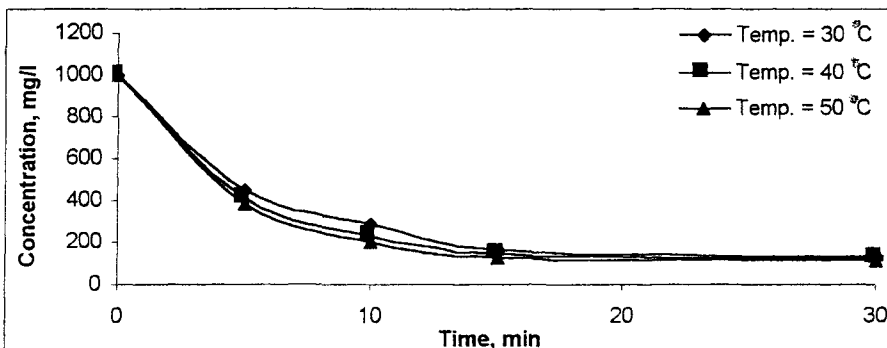


Figure 9: Concentration Vs. time at different temperatures using DIPE at 100 stroke/min & S/F = 1:1

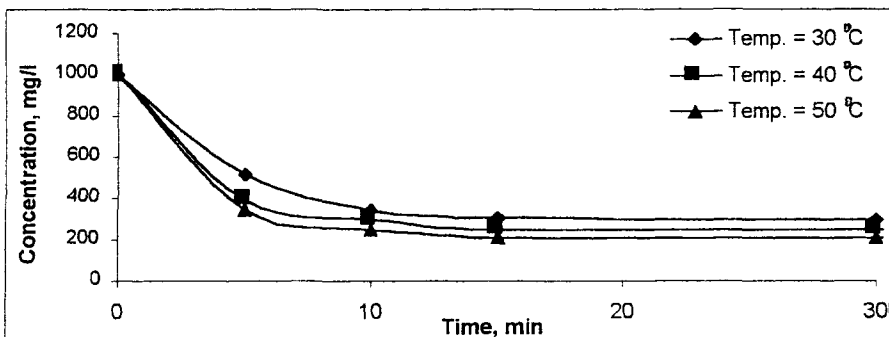


Figure 10: Concentration Vs. time at different temperatures using MIBK at 100 stroke/min & S/F = 1:1

The values of distribution coefficient found at 30 °C, 40 °C, and 50 °C are shown in figure (11) as a function of weight fraction of phenol in the organic phase. The values of K_d (equilibrium distribution coefficient) are uniformly high but are highest at low temperature, indicating that the extraction at low temperature is desirable. The values of K_d at higher phenol concentration were not investigated since it is unlikely that such concentration level would be achieved in the solvent, even for waste stream relatively rich in phenol. Data were also taken at the same temperature to determine the mutual solubility of MIBK, toluene, benzene and water. The results are in a good agreement with the results of Gross *et al.* [12]. The values which is the most important to the process are the solubility's of the solvent in water, which should be as low as possible in order to keep energy loads associated with solvent recovery low. These data would be appears to indicate that higher extraction temperatures are desirable.

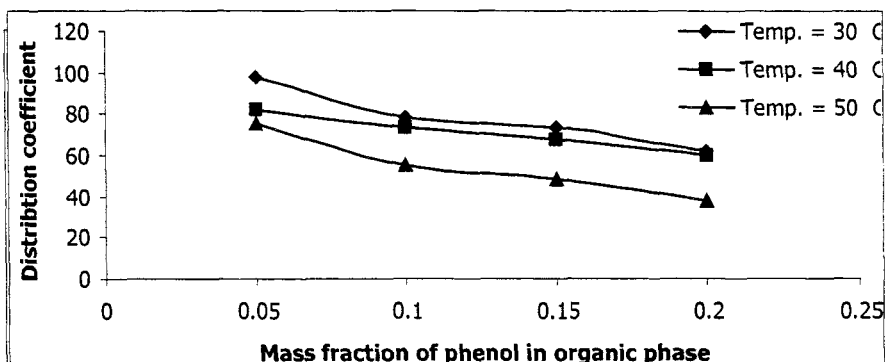


Figure 11 : Distribution coefficient for phenol between MIBK and water as a function of temperature and concentration

3.4 Effect of pH

Figure (12) show the effects of the pH on the phenol extraction process, this figure indicates that, the best extraction takes place in the pH range of (4-6), while at the alkaline range, the ability of the extraction is low. This due to that, phenol is a weak acid and dissociates into phenate ion and a proton as shown in the equation.



Phenol ionizes appreciably in aqueous solution when the pH rivals. Table (1) show the experimentally measured distribution coefficient as a function of water phase pH, phenol distributes between DIPE and water.

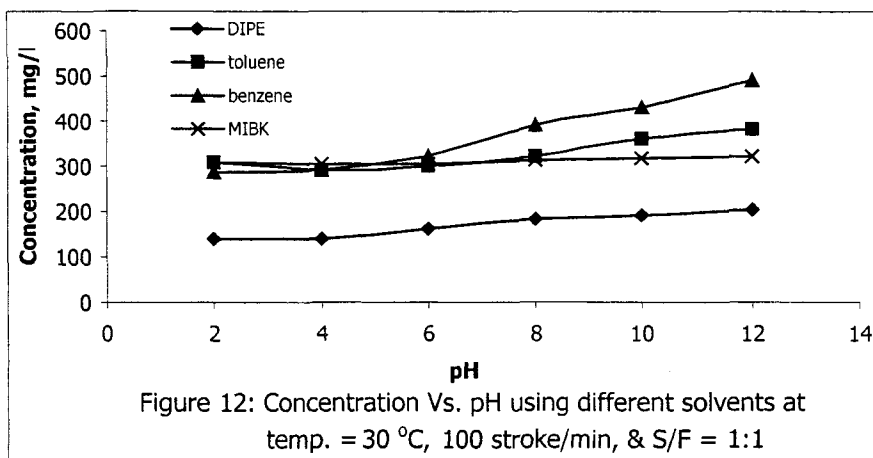
Table (1) Distribution coefficient for phenol between
DIPE and water as a function of pH at 25 °C

Water phase pH	Distribution coefficient, K_d
5	38
6	38
7	38
8	37
9	36
10	20
11	8

The distribution coefficients data are calculated from the model given by Treybal [13] for a weak acid distribute between organic and aqueous phases with dissociation occurring with aqueous phase

$$K_d = \frac{K_d \text{ low pH}}{K_a/[H^+] + 1} \quad (1)$$

Where; K_D is the equilibrium distribution coefficient, K_a is the acidic dissociation constant, and $[H^+]$ is molar hydrogen ion concentration. By using the values of K_d measured at low pH as a single adjustable parameter along with the value of K_a , there is a good agreement in the results. Since K_a is known independently, the model has only one fitted parameter. Similarly, MIBK, DIPE, toluene, and benzene found good agreement with such a model for the extraction of phenol respectively



3.5 Type of solvents

The most important factors in generation of a process for extraction of polar organic from a dilute water stream is solvent selection. Since water flows are often large, it is important to choose a solvent, which will give a high

distribution ratio for the solute in questions; this needs to keep solvent circulation rates flow becoming excessive. An effective solvent for highly polar organic frequently has a substantial solubility in water itself. In such case the dissolved solvent must be removed somehow from the raffinate water and the solvent properties must be well suited to whatever process is used for that purpose. For the lowest concentration of soluble organic in the feed water, it will be necessary to regenerate and reuse the solvent, often by distillation or stripping and chemical stability of the solvent under regeneration conditions thereby become important attributes to keep solvent consumption economically low.

There is a general rule states that “Like dissolve like”, which, should be taken into consideration in the choice decision of the solvent for the extraction process. This means that the solute and the solvent should have equal polarity, hence they should have a near value of the dielectric constant.

In this study, the solvents used are DIPE, toluene, benzene, and MIBK. Figure (13), shows the concentrations of the final aqueous solutions against time for the different solvents used at the same conditions of temperature (30 °C), S/F ratio (1:1), and 100 stroke/min. This figure indicates that; DIPE is the most suitable solvent, MIBK comes next, while all others are equally in their effect. Also, this figure indicates that the equilibrium time for all the solvents is about 15 min. After this time, the changes of the concentrations of aqueous are so small.

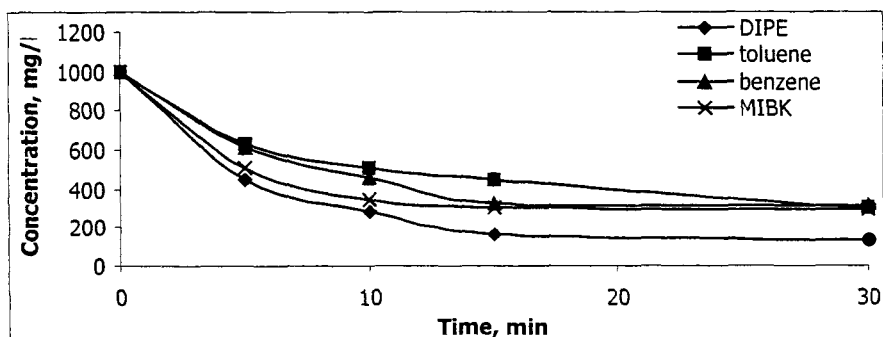


Figure 13: Concentration Vs. time using different solvents at 30°C , 100 stroke/min & S/F = 1:1

3.6 Determination of the activation energy

The activation energy is determined using Arrhenius equation:

$$K = Ae^{-E/RT} \quad (2)$$

By plotting the natural logarithm of the slopes of the first parts for the relationship of temperatures against concentrations as showing in figures (9-10) against $1/T_{\text{absolute}}$. The slope is equal to $-E/R$, where R is the gas constant. Table (2) contains the values of activation energy for the solvents used.



Table 2. The activation energy for the solvents used

Solvent	Activation energy, E, KJ/gmol
DIPE	4.216
toluene	6.89
benzene	6.16
MIBK	5.716

From table (2) it is clear that the activation energy ranges between 4 and 6 KJ/mol, which indicate that: the process is considered as physically reaction and controlled by diffusion.

4 Conclusion

In this work the feasibility for the use of simple shaker apparatus for phenol removal from aqueous solutions using different solvents were investigated. Many solvents have been used for extraction of phenol from water. The preferred solvent is whose solubility in water can be tolerated eliminating the need for further purification steps. From the results it can be concluded that DIPE give much higher value of phenol removal than other solvent. The selectivity of a solvent for a given solute depends primarily upon the nature of the solvent, the temperature of the system, and the concentration of the component involved. The maximum percent removal of phenol is 98% using DIPE at solvent to feed ratio 3:1, temperature 30 °C and 100 stroke/min., while 97% is achieved by using MIBK at the same operating conditions.

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