REMOVAL OF PHENOL FROM WATER AND WASTEWATER BY CHEMICAL PRECIPITATION WITH LIME

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ABSTRACT

The removal of high concentration of phenol from water and wastewater was studied using chemical precipitation with Iraqi manufactured lime.The procedure insured an excellent degree of phenol reduction greater than (99%). More than thirty samples of both synthetic phenolic aqueous solution and fresh industrial phenolic wastewater were used with different amounts of lime slurry.

The results of this study suggest a new approach for the removal of such toxic organic priorty pollutant like phenol using chemical precipitation method. This method is usually used for separating inoganic compounds from water and wastewater.

INTRODUCTION

The pollution of natural water resources supplies by phenolic-bearing wastes is becoming an increasingly serious problem in recent years.

Phenols are protein degenerating and highly toxic. Contact with large amount leads to death through paralysing the central nervous system. If phenol is inhaled or swallowed, local cauterizing occurs with headaches, dizziness, vomiting, irregular breathing, respiratory arrest, and finally heart failure (Goto et al., 1986; Yn et al., 1994; Knop and Scheib, 1979).

Phenols are toxic to fish as well as human at levels above (2) mg/l and can cause bad taste in fish at concentrations far below the toxic level. Sufficient concentration of phenol can deplete the oxygen in a receiving body of water since it has a relatively high oxygen demand (thoretically, 2.4 mg 0_2/mg phenol) (Lanouette, 1977; Verschveren, 1983).

Phenols are present in wastewater from oil refineries, coke plants and phenolic resin plants. At very low concentration (Less than 0.1 mol/m^3) phenol can be digested using biological treatment or chemical oxidation. On the other hand, with concentrations as high as (more than 20 mol/m^3), solvent extraction or incineration has been used for its removal. Adsorption onto activated carbon or anion-exchange resin are the effective methods for the removal of intermediate concentrations of phenol (Goto et al., 1986).

Limited information is available about the removal of synthetic organic pollutants from water and wastewater using chemical precipitation method. In separating inorganic pollutants, this method works in two ways. In the first one a chemical is added to convert the compound into a less soluble form that can be precipitates, then separated. In the other, the added chemical does not induce a chemical change but merely reduces the solubility so that the compound precipitates. This is called salting out. Both forms of application seem also possible for organic chemicals removal in general, even though polluted water with organic matters must have some of them in solution, the required reduction level of these toxic, carcinogenic substances should be below their solubility levels. Accordingly, there is little chance of precipitating them by merely reducing this solubility slightly, and the only possibility is to change them into insoluble compounds by chemical reactions. Unfortunately there is little chance of finding any chemicals that would produce insoluble compounds from the pollutants of importance (Berger, 1987; Westrick and Cohen, 1976).

The aims of this research are the following:

1. Study the performance and efficiency of chemical precipitation method using Iraqi manufactured lime to remove phenol from water and wastewater.
2. Study the effect of other synthetic organic compounds existing in phenolic waste water on the efficiency of phenol removal process.

EXPERIMENTAL WORK

Materials and methods

The materials used in this research were as the following:

1. Synthetic phenolic solution with initial concentration of (1) kg/m^3 prepared by dissolving pure crystalline phenol in distilled water.
2. Fresh samples of industrial phenolic waste water from phenolformaldeyde (novolac) resin plant.
3. Calcium hydroxide $Ca(OH)_2$ slurry (milk of lime) of (10%) concentration prepared by dissolving powdered lime in distilled water.

Experimental apparatus

The experiments were performed in (2.5×10^{-4}) m^3 (pyrex beaker) with propeller type stainless steel agitator to provide adequate mixing of phenolic solution with lime slurry.

A schematic representation of the experimental equipments is shown in figure (1).

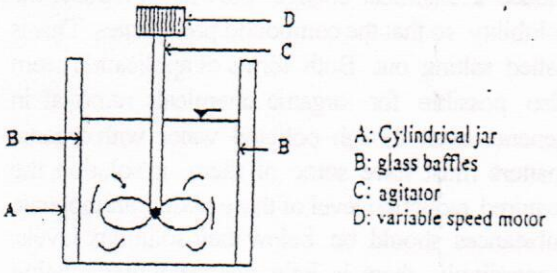

Fig. (1) Schematic representation of experimental apparatus

Experimental procedure

A standard sample volume of (1×10^{-4}) m^3 of the phenolic solution were placed in the cylindrical jars. Then different amounts of lime slurry were added to each jar. Rapid agitation of (100) RPM started and continued for (20) minutes. When the agitation period was over, the solutions were left to stand for settlement. All experiments were conducted at room temperature. Samples for analysis were obtained from each jar by pipetting of (1×10^{-5}) m^3 of the supernatant, the tip of the pipette having placed (0.05) m below the water surface.

Test methods

Two types of analysis were carried out for the examination of water and wastewater samples and as the following:

1. *Qualitative analysis:*
   Qualitative analysis was done by the researchers in accordance with (Shriner, 1980) for detection and confirmation of free phenol, formaldehyde, formic acid and methanol.
2. *Quantitative analysis*
   Pollutant concentrations were measured in the service laboratory at the department of chemistry/Collage of science/University of Baghdad by using the Gas-liquid chromatography of type (PYB UNICAN) system. Flame ionization detector (F.I.D) type was used. Hydrogen of (99.9%) purity was supplied by means of hydrogen cylinder to be implied in (F.I.D) detector to create the flame by burning hydrogen with air. Filtered and dried compressed air supplied by a compressor was utilized and nitrogen of (99.99%) purity was supplied by nitrogen cylinder to be used as a carrier gas.
   A (2) m long, (2) mm diameter glass column packed with 10% (SE-3) was used. Temperatures of column, injection and detector were 180C^0, 200C^0 and 250C^0 respectively.

RESULTS AND DISCUSSION

More than thirty experiments were conducted with lime slurry performed on the following:

1. Synthetic phenolic aqueous solution samples of (1) kg/m^3 initial concentration of phenol.
2. Fresh industrial phenolic waste water (novolac resin effluent) samples of average initial concentrations of the pollutants as follows:
   Phenol = 1 kg/m^3
   Formaldehyde = 0.3 kg/m^3
   Oxalic acid = traces

The results of these experiments were presented graphically in figure (2) as the remaining concentrations of phenol in lime treated samples were plotted versus the utilized amounts of lime.

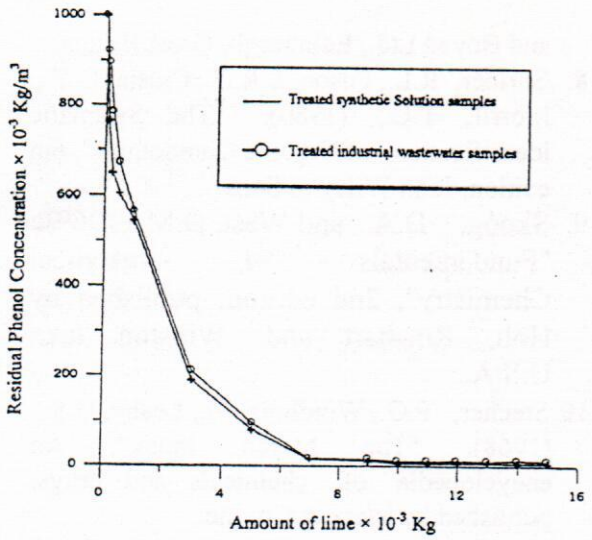

Fig. (2) Effect of lime addition on the removal of phenol in (1 x 10^{-4}) m^3 raw wastewater samples

From this figure the following can be noticed:

1. A significant removal of about more than (99%) of phenol can be obtained with lime addition of (0.01) kg to (1 $\times 10^{-4}$) m^3 of phenolic solutions.

Increasing the quantity of lime over (0.01) kg did not show any noticeable effect on the residual concentrations of phenol in a same volume of synthetic phenolic solution or industrial phenolic waste water.

This may be attributed to the fact that when a chemical reaction attains equilibrium, a state of dynamic equilibrium has been reached and the reaction will no more proceeds far to the right (Pine, 1987; Skoog and west, 1969).

Removal of phenol from the phenolic solutions was accomplished by the reaction of lime with free phenol (C_6H_5OH) forming a pink reddish powder precipitate of calcium phenolate ($C_6H_{10}O_2Ca$) and according to equation (1).

$$Ca(OH)_2 + 2C_6H_5OH \rightarrow C_{12}H_{10}O_2Ca + 2H_2O \quad (1)$$

2. The remaining concentrations of phenol in the treated synthetic phenolic solution samples are slightly less than in the treated industrial wastewater.

This might be attributed to the presence of other organic compounds which may interfere and consume lime to lesser or greater degree with phenol. This was approved by the analysis of the chemically treated industrial effluent samples as shown in table (1).

Table (1) Initial and final concentrations of pollutants in industrial waste water samples

Type of pollutant	Average initial concentrations (kg/m^3) before the chemical treatment	Average final concentrations (kg/m3) after the chemical treatment
Phenol	1	0.01
Formaldehyde	0.3	2×10^{-4}
Oxalic acid	Traces	Nil

From table (1) the following can be seen:

I. The highly reduction of formaldehyde in the treated sample can be attributed to the fact that formaldehyde polymerises in the presence of weak alkalis, e.g., clacium hydroxide, to a mixture of sugars of formula $C_6H_{12}O_6$, which is known as formose of α-acrose according to equation (2) (Schmidt and Rule, 1950; Finar,1967).

$$H.CHO+H.CHO+H.CHO+H.CHO+H.CHO+H.CHO \rightarrow \underset{\text{(formose)}}{CH_2OH.CHOH.CHOH.CHOH.\ CHOH.CHO} \quad (2)$$

II. The reduction of oxalic acid in the treated industrial effluent sample was due to the formation of cubic crystals of insoluble hydrated calcium oxalate (Stecher et al, 1968) according to equation (3).

$$C_2H_2O_4 + Ca(OH)_2 \rightarrow CaC_2O_4.\ 2H_2O \quad (3)$$

CONCLUSIONS

The conclusions that can be drawn from the experimental work of this research will be as follows:

1. chemical precipitation method using lime insured a good degree of phenol reduction in water and waste water greater than 99%.
2. Results of lime treatment experiments indicated that the reduction of phenol depend on the utilized amount of lime for certain initial phenol concentration and also on the existence of other organics with phenol which may consum lime.
3. Using chemical precipitation with lime for the reduction of high concentration of phenol considered to be an efficient and economic method for treating phenolic-bearing wastes since lime is a cheap locally manufactured material.

4. The solid phenolic sludge resulted from the chemical precipitation by a gravity sedimentation then it must be dewatered and burned.

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