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Research Article

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Effect of process parameters on the phenol removal rate from petrochemical effluents using electrochemical method

Srinivasulu K.[1*], Balasubramani K.[2] and Manisha Vidyavathy S.[1]

[1]Department of Ceramic Technology, Alagappa College Technology Campus, Anna University, Chennai, Tamil Nadu, India
[2]Department of Petrochemical Engineering, JCT College of Engineering and Technology, Coimbatore, Tamil Nadu, India

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ABSTRACT

The present work is to degrade the phenolic waste from petrochemical industry by electrochemical method using Titanium doped with SnO_2-Sb as anode and AISI 305 stainless steel as cathode. The degradation rate depends on the current supplied and the rate of agitation of the cylindrical stainless steel cathode rod placed inside Hexagonal shaped Titanium anode. Experimental studies were conducted in stagnant condition and parameters like pH, current density, temperature, initial concentration and cathode speed were varied. The phenol removal rates possess its maximum at pH 3 and began to decrease at pH 5 and pH 6. It was observed that the phenol degradation rate increased with increase in current density, electrolysis temperature and cathode speed. High initial concentration of phenol was found to undergo relatively lesser mineralization.

Keywords: Electrochemical treatment, phenol degradation, petrochemical industry effluents

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INTRODUCTION

A wide variety of synthetic organic compounds have been brought into the environment by human activities, and many organic compounds are contaminating the ground and surface water. Many industries use phenolic materials in their manufacturing processes. Phenol is also used in the production of drugs, weed killers and synthetic resins. Phenol and its derivatives are also present in the wastewater of industries like coking, paint dyes, wine distilleries, synthetic rubber, textiles pharmaceuticals, solvents, manufacture of pesticides, paper and wood etc [1 – 2]. Occupational exposure to phenol has been reported during its production and use, as well as in the use of phenolic resins in the wood products industry. It has also been detected in automotive exhaust and tobacco smoke [3]. Toxic organic contaminants such as heterocyclic and phenolic compounds, causes serious environmental risks and should be eliminated before discharge into natural water bodies. Over 2mg/L phenol concentration is toxic to fish and concentration between 10 to 100 mg/L would result in death of aquatic life within 96 hours.

Phenol and its vapour are corrosive to eyes, skin and respiratory tract. Repeated or prolonged skin contact with phenol may cause dermatitis or even second and third degree burns due to phenol’s caustic and defatting properties. Inhalation of phenol vapor may cause lung edema. The substance may also cause harmful effects on the central nervous system and heart, resulting in dysrhythmia and coma. Many technologies have been investigated for the degradation of phenolic compounds and are well known to be characterized by higher salinity, acidity, chemical oxygen demand value and low biodegradability which means that the effluent cannot be treated by the conventional process [4 – 5]. The phenolic compounds in the industrial effluents that are not removed by biological treatment can be eliminated by advanced waste water treatment methods, among which the most frequently used is the Fenton process. Despite the substantial effectiveness of the process in removing organics and surfactants, it has some drawbacks, such as production of large quantities of sludge, the consumption of chemicals and the necessity of acidic condition. Other technologies for the treatment of phenolic compounds include the use of ozone gas or ozone and UV radiation [6]. However the cost of ozone still remains an important drawback of the process.

Electrochemistry is becoming a new alternative for water treatment and is replacing the traditional process. Electrochemical oxidation of various types of wastewater including the phenolic wastewater has been investigated by a lot of researchers [7]. With unique features such as simplicity, robustness in structure, high degradation speed, effective, selective, easy to control and safety, it is possible that the electrochemical process can be developed as cost-effective technology for the treatment of aromatic pollutants [8 – 9]. Electrochemical reaction can effectively oxidize toxic organics [10]. The effectiveness of electrochemical wastewater treatment depends on the nature of anodes that are used in the process [11]. Traditional electrodes, such as graphite and nickel show a poor current efficiency in organic degradation [12]. Dimensionally stable anodes (DSAs) that are prepared by the deposition of a thin layer of metal oxides on a base metal, usually titanium are found to have varying degree of success. The widely used RuO_2 and IrO_2 based coating surface does not appear to have a high reactivity of organic oxidations [10]. Other coating materials such as PbO_2^- and SnO_2^- based coatings have been introduced to improve the treatment performance. PbO_2 electrodes can be highly effective for complete organic destruction [13].

Hence PbO_2 and similar anodes are considered to have sufficient electrocatalytic capacity for organic oxidation [14]. However concern over the possible toxicity of Pb leaching the working anode would hinder the actual application of PbO_2 anodes. The SnO_2 based coatings have shown a similar reactivity as that of PbO_2 for electrochemical organic degradation [12, 15]. SnO_2 coatings are expected to offer a better solution for the enhancement and application of electrochemical process to organic degradation. The electrochemical pre-treatment of electrode surface has been shown to reduce fouling. In general, the oxidation of phenolic compounds produces phenoxy radicals that can be further oxidized to hydroquinone and then into benzoquinone. Subsequent oxidation of these products, after opening of the aromatic ring, leads to the formation of aliphatic carboxylic acids [16].

Researches on anodic organics oxidation have been largely reported [17]. The anodic oxidation mechanism is

$$MO_x\,(H^+) + H_2O_{\,ads} \longrightarrow MO_x\,(^{\cdot}OH)_{\,ads} + H^+$$
$$MO_x\,(^{\cdot}OH)_{\,ads} + R \longrightarrow CO_2 + H_2O$$

Where MO_x is one of the metal oxides like Tin oxide (SnO_2). R is one of organic pollutants.

In recent years, researchers have paid attention on the cathodic organic degradation, especially on the cathodic indirect organics oxidation.

The mechanism is followed [18]

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$$
$$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2\,OH^-$$
$$H_2O_2 + R \longrightarrow CO_2 + H_2O$$

Based on the above background the present study focuses on the study of the degradation of an aqueous phenol solution by an electrochemical reactor made up of hexagonal shaped titanium anode with dimensions of (6 x 7.5) cm^2 doped with SnO_2-Sb. Moreover to accelerate the rate of phenol degradation, a cylindrical stainless steel (AISI 305 Grade) was taken as cathode and rotates inside the anode. Anodic-cathodic electrochemical system is an important research direction in the treatment of wastewater by electro chemical method.

EXPERIMENTAL SECTION

2.1 Electrode Surface Preparation

The titanium anode doped with SnO_2– Sb is used as anode for the study of phenol oxidation. Ti/ SnO_2– Sb are selected because of its electro catalytic activity thus enhancing the rate of oxidation. Titanium anode of hexagonal shaped with dimensions of (6x7.5) cm^2 and 1mm thickness was taken and polished thoroughly with 320 grit sand paper. Cylindrical stainless steel (AISI 305 Grade) of dimension (2x7.5) cm^2 is taken as cathode and is rotating type. It is thoroughly polished by sand paper to remove any impurities on its surface.

The process of electrode preparation was carried out in four steps:

2.1.1. Degreasing:

The hexagonal Ti anode is degreased by immersing them in 40% NaOH solution for 2 hours at 80^0C. This was done to remove any surface impurities sticking to the plates. After degreasing, the plates were washed with de-ionized water.

2.1.2. Etching

The degreased anode is then etched in 15% oxalic acid solution at 98^0C for 2 hours followed by thorough washing with de-ionized water. The etched plates became grey in color losing their metallic sheen. This was carried out to create micro-pores on the surface of the plate for proper adherence of the SnO_2– Sb coating.

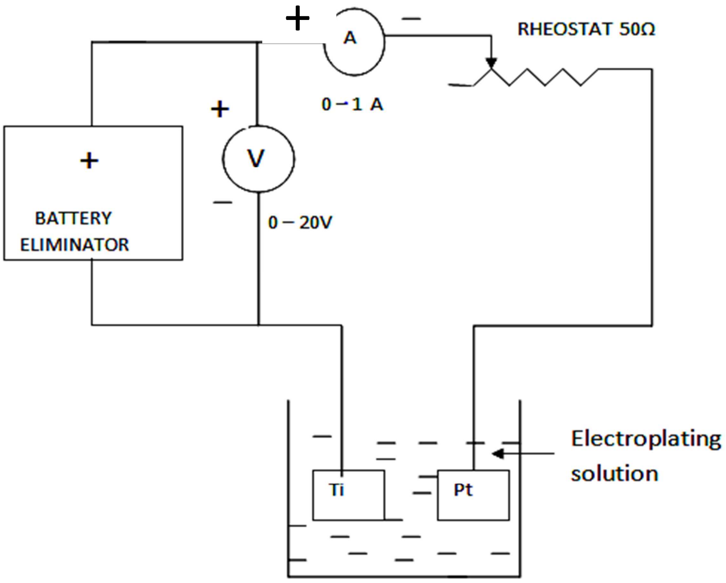
2.1.3. Electro-deposition

The Ti/SnO_2– Sb electrodes were prepared by electro-deposition for the inner coating layer. During this process the Ti anode was placed as the cathode in 100ml of n-butyl alcohol solution containing 17.5gm of $SnCl_4.5H_2O$, 0.73gm Sb_2O_3 and 2 ml concentrated HCl (35%). A constant DC supply of 0.12 A was charged from a battery eliminator for 25 minutes for electroplating the cathode using silver as the counter electrode is shown in Fig. 1

Then the inner coating layer on the titanium plate was dried in a furnace at 400^0C for 2 hours. This inner plating was found to be essential for the improvement of the durability and stability of the SnO_2– Sb coating on the surface.

2.1.4. Thermal Deposition

The electrodeposited Ti/SnO_2–Sb electrode was prepared by thermal deposition of the outer coating layer. During this process the plate was dipped into a coating solution that consisted of 30g of $SnCl_4.5H_2O$, 0.8g Sb_2O_3 and 2.5ml of concentrated HCl (35%) in 50ml n-butyl alcohol**.** After five dipping drying cycles at ambient temperature, the Ti plate was annealed in a muffle furnace at 550^0C for 2 hours. The above procedure was repeated five times to produce the final Ti/SnO_2– Sb anodes.



2.2. Phenol Electrolysis for Electrochemical method

Electrochemical oxidation of phenol was conducted in an undivided reactor. This experimental setup is shown in Fig. 2. The hexagonal shaped titanium doped with SnO_2-Sb (6 x 7.5) cm^2 anode and a cylindrical stainless steel (AISI 305 Grade) (2 x 7.5) cm^2 cathode were concentrically assembled each 2 cm apart into the electrolytic cell with a final volume of about 1000 ml. The supporting electrolyte of 0.25M Na_2SO_4 and certain concentration of phenol pollutant was pumped through the reactor and then returned to the reservoir for recycling. A constant DC supply of 0.36A was applied through the pair of electrodes which resulted in a current density of 7.5 mA/cm^2 and a constant voltage of 7V. The solution was stirred by the cylindrical cathode for maintaining constant ambient temperature without any special control measures. Experimental parameters like current density, initial pH, temperature, initial phenol concentration and cathode speed was varied during the experiment. Samples were withdrawn for analysis of the phenol concentration at certain intervals during the degradation process. Concentration of phenol was measured by 4-amino-antipyrine titration. From the intermediate concentration of phenol and the percentage degradation of phenol is calculated by the formula.

Phenol degradation (%) = $\{C_O - C/C_O\}$ X 100,

Where C_O and C are the initial and final concentration respectively.

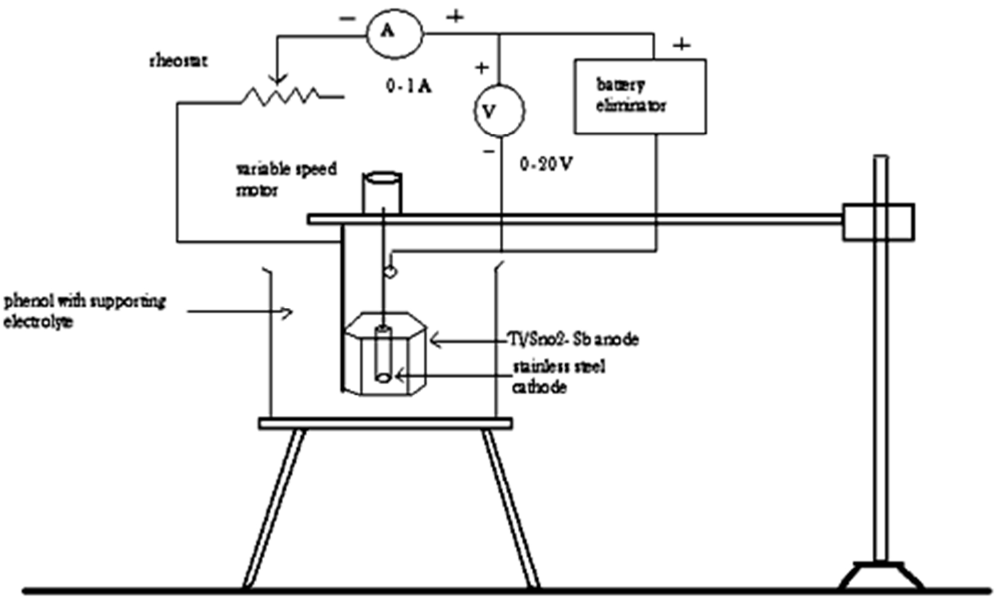


Fig.2. Circuit diagram for phenol electrolysis for electrochemical method

RESULTS AND DISCUSSION

3.1. Effect of pH on phenol degradation

It has been established that pH is the most important operating factor influencing the performance of an electrochemical process. The effect of initial pH (selected pH 2, 3, 4, 5, 6) of 500 ppm phenol solution on the degradation of phenol was tested over a period of 270 minutes reaction time as shown in Fig 3. The initial pH of the solution was adjusted using sulfuric acid. The phenol removal rates possess its maximum at pH 3 and then begin to decrease at pH 5 and pH 6. Since the anode is perfectly stable in acid medium, no attempt was made to explore the phenol degradation in higher alkaline medium. Low pH could inhibit the occurrence of oxygen evolution reaction, in order to promote anodic oxidation. At the same time acidic conditions were more conducive to produce hydrogen peroxide, which could be decomposed into hydroxyl radical. At pH 3, the phenol removal rate reached 98.0% as shown in Fig. 4. The increase in the pH from 6.7 to 7.2 was noticed in the beginning and latter the pH remained constant during the whole run due to the production of acid compounds. The acids seem to be the most critical compounds to be mineralized, likewise for the formed intermediate reaction products such as aromatics.

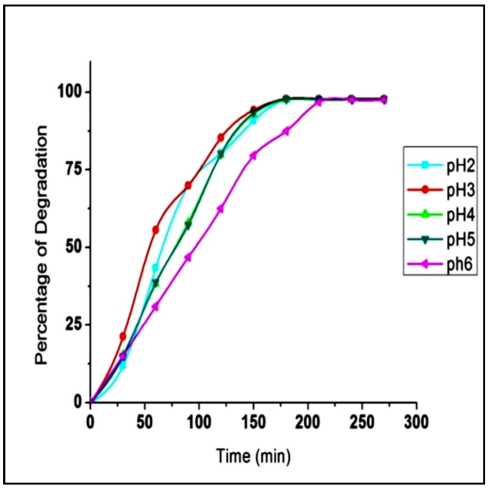


Fig.3. Variation of phenol degradation with time at different pH values

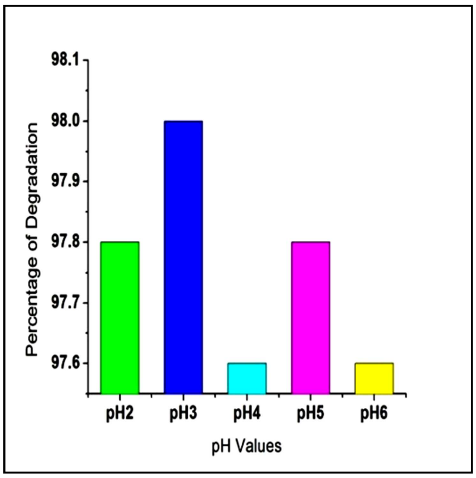


Fig.4. Effect of pH on phenol degradation rate

3.2. Effect of Current Density on phenol degradation

Current density is one of the influential factors in electrochemical oxidation of organic effluents, which plays a key role in the output of the electronics. Oxygen evolution from the anodes is also a major competitive reaction in the electrochemical oxidation. Fig. 5 shows the variation of phenol degradation with time at different current densities ranging from 2.5 to10 mA/cm^2. It was found that at a current density of 10 mA/cm^2 and after 3 hrs of degradation process, phenol removal rate reached 98.0% as shown in Fig. 6. It was noted that increasing to current density can produce more electronic, promoting the generation of OH$^-$ and reduction of oxygen. However, it also seen that with increased current density, the current efficiency was reduced. Comprehensively considering the removal rate, current efficiency and energy consumption a valve 10 mA/cm^2 was chosen as a suitable current density for degradation system. Therefore phenol removal is more likely to be degraded to organic acids and will be faster at higher current density. The application of the highest current density can be suggested in order to obtain the complete abatement of the organic content in short time. Thus the degradation process has been turned into the so called electrochemical cold combustion. Obviously, higher degradation rate can be achieved at higher current density. Phenol removal rate is rapid at high current density and low initial phenol concentration.

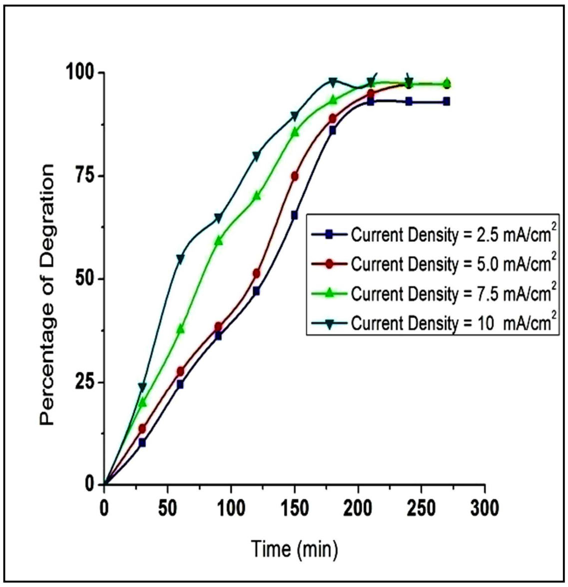


Fig.5. Variation of phenol degradation with time at different current densities

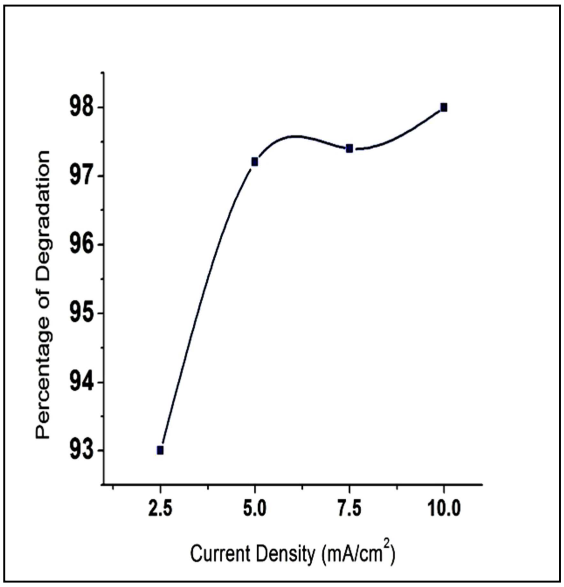


Fig.6. Effect of Current density on phenol degradation rate

3.3. Effect of temperature on phenol degradation

The electrochemical reaction of phenol is highly temperature dependent and shows that an increase in temperature will strongly facilitate the degradation of phenol. Fig. 7 shows a series of experimental runs performed at different temperatures say 40, 45, 50, 55 ^{0}C. A temperature of 55 ^{0}C could improve the degradation to high level after 3 hrs of electrolysis period. The rise of temperature as enhanced the molecular motion velocity and catalytic activity of the electrodes, which in turn speeds up the reaction. At temperature of 55 ^{0}C the degradation was higher when compared to 40 ^{0}C as shown in Fig. 8. An increase in the temperature led to more efficient process. However, there is no need for heating wastewater at much higher temperatures in practical application due to increase in energy consumption. Similar results were obtained for phenol degradation, i.e. complete removal of phenol 98% was achieved during the first 3 hrs duration. Higher temperatures appear more detrimental to phenol degradation than do lower temperatures. Therefore it might be convenient to operate at higher temperatures for the complete removal of phenol. The main influence of the electrolysis temperature on the degradation system was the production of hydroxyl radical and the catalytic activity of the electrode.

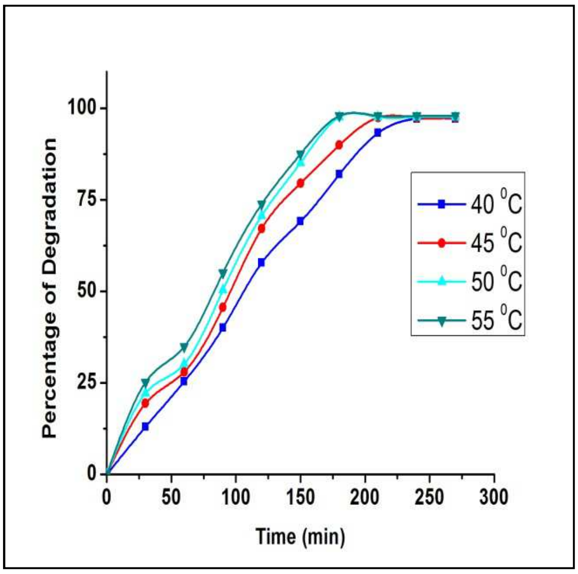


Fig.7. Variation of phenol degradation with time at different electrolysis temperatures

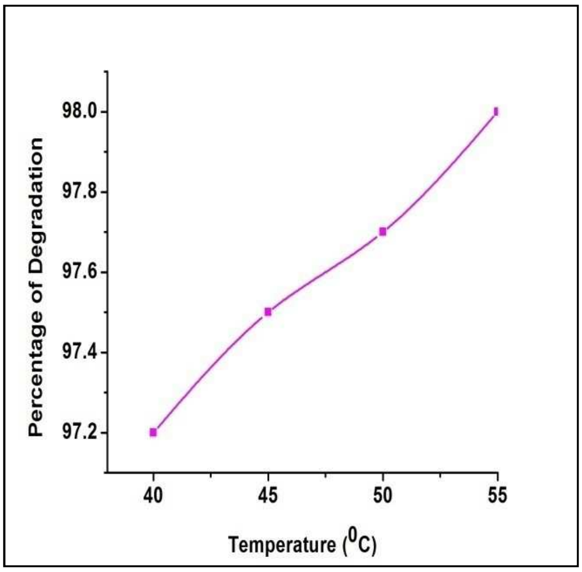


Fig.8. Effect of temperature of phenol degradation rate

3.4. Effect of initial concentration on phenol degradation

The effect of initial phenol concentration was studied at five different initial concentrations say 100, 200, 300, 400, 500 ppm. It was observed that the degradation of phenol takes place quickly during the initial stages and almost complete mineralization was achieved with a degradation rate of 92.2% after 1.5 hrs electrolysis period as shown in Fig. 9. The higher initial concentration of phenol was found to undergo relatively lesser mineralization. Fig. 10 shows that the phenol removal rate linearly increases with increase in the initial phenol concentration. It is clear that complete phenol removal was achieved on high concentration of phenol as the electrolysis time was extended. At current density of 8.5mA/cm^2 with Na_2SO_4 as supporting electrolyte, the phenol concentration decreased from around 20, 40 and 80 ppm to zero after 30, 60 and 90min, respectively. The electrolysis time for complete removal of phenol was proportional to the concentration of phenol. In conclusion, the Ti/SnO_2–Sb anode performs well for electrochemical degradation of high concentration of phenol solution with appropriate current density and Na_2SO_4 as supporting electrolyte.

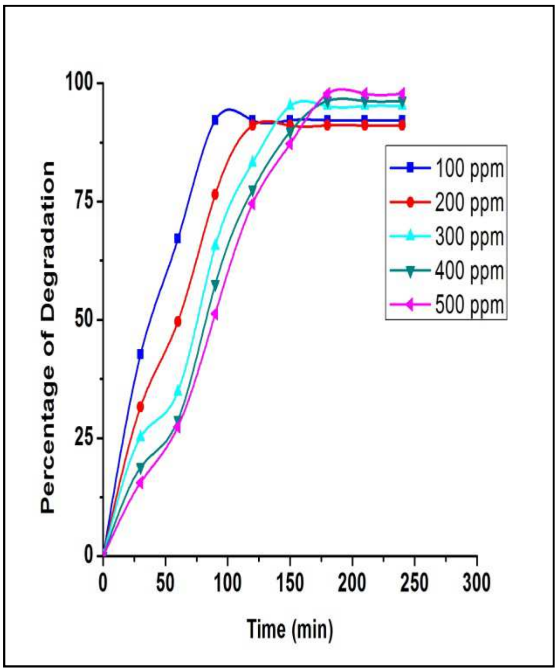


Fig.9. Variation of phenol degradation with time at different initial concentrations

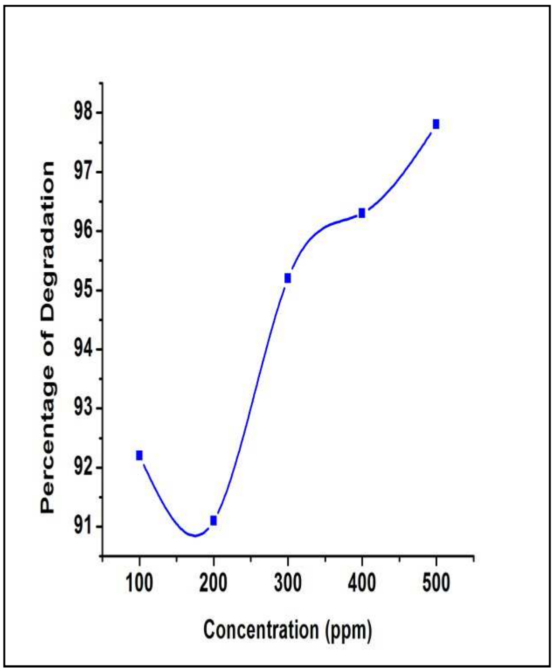


Fig.10. Effect of initial concentration on phenol degradation rate

It has been found that the cathode speed is an important operating factor influencing the performance of electrochemical process. The effect of cathode speed was studied at four different speeds say 250, 400, 600 and 750 rpm. The cathode speed was adjusted using a speed regulator. A cathode speed of 750 rpm could improve the degradation to high level in of 97.6% after 150 min electrolysis period is shown in Fig. 11. The rise of cathode speed enhanced molecular motion velocity and catalytic activity of the electrodes, which speed up the reaction. Fig. 12 shows that higher cathode speed of 750 rpm shows higher degradation when compared to reactions at 250 rpm. An increase in the cathode speed lead to more efficient process.

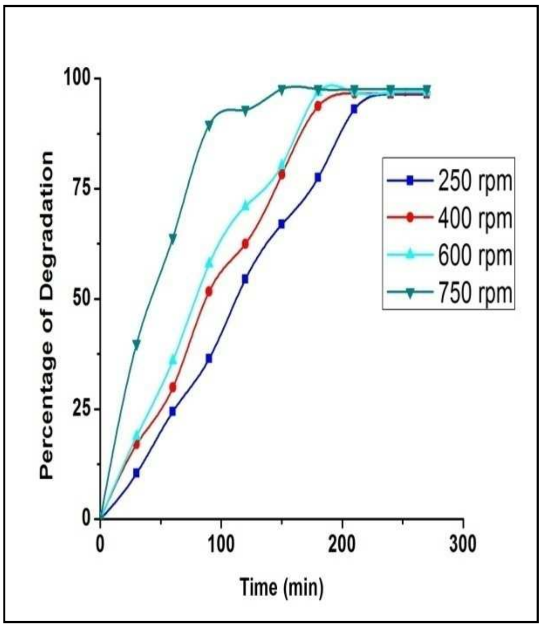


Fig.11. Variation of phenol degradation time at different cathode speeds

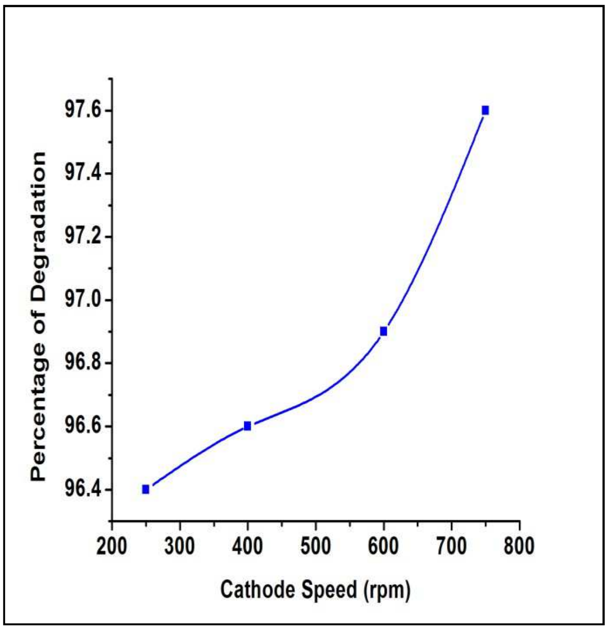


Fig.12. Effect of cathode speed on phenol degradation rate

CONCLUSION

Electrochemical degradation of Phenol using titanium anode with sodium sulphate as an electrolyte is used to treat the petrochemical industrial effluents. Degradation rate depends upon electrode surface area, supporting electrolytes, current intensity, agitation and electrolysis temperature. Degradation rate of phenol begins by formation of intermediate compounds like Hydro-Quinone, Benzo-Quinone and then it is converted into malic acid. The pH falls from base character to acidic. Optimization is done with different concentration using varying parameters like pH value, current density, speed of the cathode and temperature. The experiment was conducted by using the above parameter and the rate of degradation of phenol was detected. The phenol removal rate possess its maximum at pH 3 and then begins to decrease at pH 5 and pH 6. Since the anode is perfectly stable in acid medium, no attempt was made to explore the phenol degradation in higher alkaline medium. Low pH could inhibit the occurrence of oxygen evolution reaction, in order to promote the anodic oxidation. At pH 3 the phenol removal reached 98.0%. For a current density of 10 mA/cm^2 and after 3hrs degradation, phenol removal reached 98.0%. The reason is that increasing of current density can produce more electronic, promoting the generation of OH$^-$ and reduction of oxygen. However it also seen that with increased current density, the current efficiency was reduced. A temperature of 55 ^{0}C could improve the degradation to a high level after 3 hrs of electrolysis period with a degradation rate of 98.0%. The rise of temperature enhanced molecular motion velocity, which speed up the reaction. Degradation of phenol takes place quickly during the initial stage and almost complete mineralization was achieved with a degradation rate of 92.2% after 1.5hrs. High initial concentration of phenol was found to undergo relatively lesser mineralization. It was observed that phenol removal rate linearly increases with increases in initial phenol concentration. The cathode speed of 750 rpm could improve the degradation to high level in which 97.6% was achieved after 2.5 hrs electrolysis period. The rise of cathode speed enhanced molecular motion velocity and catalytic activity of the electrodes speeds up the reaction.

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