Electrochemically Generated Aluminum-Species for Remediation of Waste Water containing 2, 4-Dichlorophenol

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ABSTRACT

An Effective treatment process for 2,4-dichlorophenol (2,4-DCP) in wastewater is highly essential, since it may cause great threat to our environment. In such context,a low-cost potential and environment-friendly technique has been demonstrated for the removal of a toxic compound 2,4-DCP from aqueous media.The electrochemically generated aluminum sorbent was used to remove 2,4-DCPfrom waste water by in-situ electrocoagulation and by adsorption. The experimental findings were analyzed based on the percent removal of 2,4-DCP with time. DCP-containing wastewater was electrocoagulated in a two-electrode monopolar electrocoagulation cell with aluminum as the sacrificial anode and 0.05 M NaCl as the internal electrolyte, with the electrolyte concentration kept constant throughout the experiment. Starting concentration and pH were found to have a significant impact on the electrocoagulation process for removing 2,4-DCP from wastewater.

Keywords: Aluminum sorbent, 2,4-Dichlorophenol (2,4-DCP), electrocoagulation, adsorption,sacrificial anode.

1. INTRODUCTION

Phenolic compounds are present in different industrial effluents, including those from the production of chemicals, petrochemicals, medicines, textiles, and food poses a significant risk to the environment for several reasons. Firstly, phenolic are known to be toxic to a wide range of organisms, including plants, animals, and microorganisms. They can inhibit the growth and development of plants, disrupt the reproductive systems of animals, and cause cell damage in various organisms. They can harm the kidney, liver, and pancreas in addition to being hazardous to the majority of aquatic organisms and human. They can also induce protein denaturation, tissue erosion, and paralysis of the central nervous system. Exposure to these toxic substances can lead to chronic diseases, such as cancer, as well as acute poisoning symptoms like nausea, vomiting, and respiratory distress [1-4]. They are toxic even at low concentrations. Phenol is corrosive and can penetrate through the skin. Spilling liquid solution on even small areas of the skin can be fatal. Its contact may cause no immediate pain but later intense burning sensation is felt. Other symptoms are bad headache, dizziness, muscular weakness and dimness of vision and hearing. Individual phenol and chlorophenols should not be present in drinking water at a level above 0.1 ppb. Certain phenolic compounds are potentially hazardous to aquatic wild lives.Chlorophenols are poisonous substances that are released into the environment as a result of commercial or agricultural operations. Fish and other aquatic species can absorb chlorophenols through their skin, gills, or digestive systems. A maximum average 2,4-dichlorophenol concentration in surface waters shouldn't be more than 2.02mgL^{-1}, according to the US EPA[5]. The aquatic environment may contain chlorophenols in a variety of ways. They can be transported in biological tissues, dissolved in free or complexed form, adsorbed on benthic sediments or suspended inert solids. About 50% fish likely to die at 1.0-2.0 ppm phenol in water. Adsorption is considered to be an important process in the transport of organic pollutants, including phenols. Cholophenolates were found to be chemisorbed on oxide surfaces via an inner sphere co-ordination and also found to be absorbed physically as cholorophnolate ion and the cholorophnols as self-associated molecules.

The majority of phenolic compounds is poisonous and has the ability to persist in the environment for extended periods of time. High amounts of chlorophenols during pregnancy caused female rats to have fewer offspring and smaller babies when they gave birth. This suggests that exposure to chlorophenols during pregnancy can have adverse effects on reproductive outcomes, potentially impacting the health of the offspring. Secondly, 2,4-DCP, a specific type of chlorophenol, is described as toxic and has been linked to severe health problems in numerous reported cases[5].

A male worker was died instantly after exposed to hot, compressed vapor that included 2,4-DCP (the quantity and purity are unknown)[6]. Additionally, it has been claimed that a worker who had less than 10% of his body surface splattered with nearly 100% pure molten 2,4-DCP died after experiencing an epileptic seizure within 20 minutes of the incident. There were, respectively, 24.3, 5.3, 18.7, and 1.2 mg/L of 2,4-DCP found in his serum, urine, bile, and gastric content[7]. In 1998, another worker who was sprayed with hot, compressed steam containing 2,4-DCP (the quantity and purity are unclear) passed away an hour after becoming unconscious. His forearm, knee, thigh, and face were contaminated, and amounts of 2,4-DCP of 13.1 and 6.2 mg/L in serum and urine, respectively, were found[10].This indicates that 2,4-DCP (2,4-Dichlorophenol) can be quickly absorbed through the skin if a person comes into touch with molten or heated 2,4-DCP (2,4-Dichlorophenol). If the injured skin areas are not immediately washed with water, the amount absorbed can be fatal to humans, even if only 1% of the body's surface area is exposed to molten 2,4-DCP (2,4-dichlorophenol [6,7]. The US EPA together with OSHA issued warning of CANPR (Chemical Advisory and Notice of Potential Risk) for 2,4-DCP[6].A number of technologies are known to have been applied to control pollution caused by phenolic compounds[1]. These are, (a) Adsorption; (b) Hydrolysis;(C) Photo catalytic degradation; (d) Chemical oxidation; (e)Chlorination; (f) Liquid membrane permeation etc. A new and versatile technique known as electrocoagulation based on electrochemical (EC) principle is currently been tried in many countries. In the present study both adsorption as well as electrocoagulation have been used. A suitable anode material is electrolytically oxidized to produce the coagulant in situ during the EC process. By allowing them to react (i) with an ion that has the opposite charge to their own, or (ii) with a floc of metallic hydroxide produced in the effluent, charged ionic species, whether they be metals or not, are eliminated from wastewater using this method.

2. EXPERIMENTAL DETAILS

In the present research synthetic wastewaters containing DCP were selected for investigations. All the chemicals and reagents used are of pure analytical grade and used without further purification.

2.1 Preparation of Al-sorbent

Al-sorbent was prepared by electrocoagulation carried out by using two electrode electrocoagulation cell (Fig. 1).
This setup includes the electrode assembly, a DC power supply unit, a voltage stabilizer, a resistance box to regulate the current and a multimeter to read the current values. The electrode assembly consisted of pairs of conductive metal plates placed in parallel arrangement. In this experiment, the plates of aluminum (7 cm × 7cm × 0.15 cm) were used and the anode is commonly known as "sacrificial electrode".

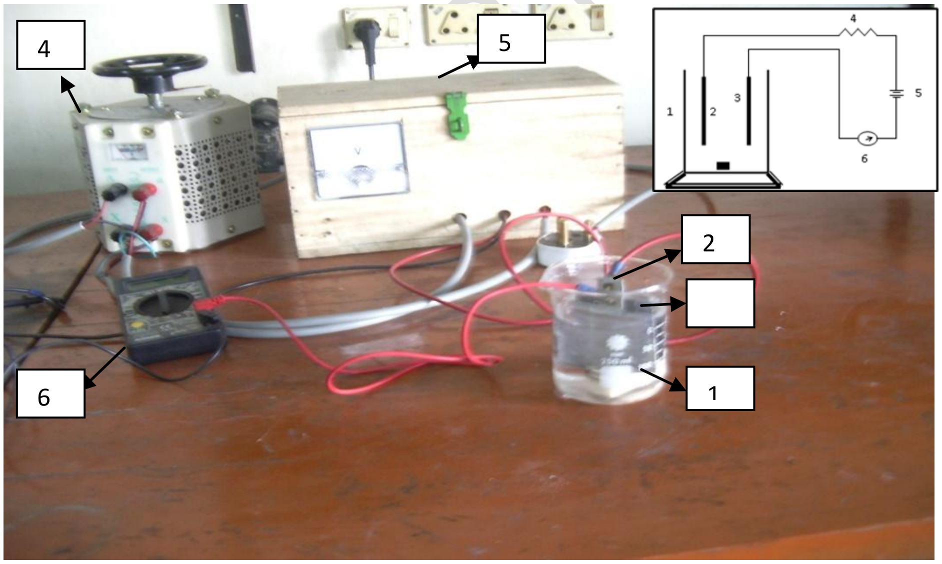

Fig. 1. Photograph of EC-cell used in the present work [Schematic diagram of the Electrochemical (EC) cell is shown inset] 1. Pyrex beaker; 2. Al-Anode; 3. Al- Cathode; 4. Variable resistance; 5. D.C. source; 6. Ammeter

In this series of experiment 500 mL of 0.05 M aqueous NaCl (99.5%) solution was taken in a 1000 mL beaker and the electrodes were immersed into it. An electrode holder made of ebonite kept the anode and cathode separated by definite distance (2.2 cm). Anode and cathode were fully immersed in the electrolytic solution. The pH of the solution was found to be 5.58 while the pHof the solution after the experiment was 8.91. Electrolysis was then carried out for a predetermined time when suspension of oxyhydroxides was generated in the electrolytic solution. Usually, a current of 3 A was used for electrolysis.At the end of each run, the suspension was kept in open air for 24 hours to settle completely and then filtered through a 2.5 μm pore size membrane filter and the recovered solid was washed with distilled water until free from chloride. After drying in air, the Al-sorbent was dried in an oven at ~383 K for 4-5 hours.

2.1 Adsorption on Al-sorbent

The adsorption experiments were carried out in batch mode under different conditions of DCP concentration and pH of the solution Adsorption experiments were carried out by using 0.2g of Al-sorbent and 25 mL of 2,4-DCP solution in each of the 10 bottles at a constant pH. The pH of the experimental solutions was maintained constant by adding acid or alkali where necessary, and the volume of acids or alkali added was kept minimum in order to avoid dilution of the adsorbate solution. The bottles were shaken in a thermostatic mechanical shaker at 29^{o}C. After a definite interval of time each bottle was withdrawn. The supernatant of the content was transferred and centrifuged separately until a clear liquid was obtained and the pH of the content was adjusted. The absorbance of the clear solution was measured spectrophotometrically. The adsorption time were varied from 20 minutes to 110 minutes. The concentrations of DCP in wastewater were determined spectrophotometric ally. The % of DCP adsorbed or removed was calculated from the following relationship:

$$\% of\ DCP removed = \frac{C_0 - C_t}{C_0} \times 100$$

Where, C_0 and C_t are the concentration before and after adsorption.

2.2 In- situ electrocoagulation

In-situ electrocoagulation of 2,4-DCP was carried out by using two electrode electrocoagulation cell containing Al as “sacrificial” electrode (7.0cn ×7.0cm× 0.1cm). 400 mL of definite concentration of 2,4-DCP solution was taken in an electrolytic cell and the pH of the solution at this stage was 5.85. During electrocoagulation 1.0 A current was applied and the solution was collected at definite time interval and the process was continued for about an hour. Collected solution was filtered and pH was adjusted to ~5.85. The absorbance of the clear solution was measured spectrophotometrically. The % of DCP removed was calculated by using the following equation-

$$\% of\ DCP removed = \frac{C_0 - C_t}{C_0} \times 100$$

Where, C_0 and C_t are the Concentration of DCP before and after electrocoagulation

2.3 Solvent extraction of the products

500 mL of 500ppm 2,4-DCP solution was taken in an electrolytic cell with Al- electrodes. Electrocoagulation was carried out by 2 A current. The process was continued for one hour. After electrocoagulation the solution was filtered. The solution was colorless before electrocoagulation, but changed to orangecolor after electrocoagulation (Fig. 2.). A 100 mL sample solution (filtrate) was taken into a separating funnel (500 mL) and about 50mL of diethyl-ether solution was added to it and shaken for 15 minutes manually and settle for about 1 hour. The organic layer formed at the upper portion of the funnel was taken out and extraction was repeated twice. The clear organic solvent extracts were made water free by adding anhydrous sodium sulfate (Na_2SO_4). Then the organic solvent was totally water free and it was filtered by using Whatman filter paper. Evaporation of the solution was carried out under reduced pressure using rotatory vacuum evaporator with bath temperature not exceeding 40^{o}C. The gummy sample was then completely dried by freeze-drying and collected in a vial for further analyses.

3. RESULTS AND DISCUSSION

The Prepared Al-sorbent was previously characterized [8]. The sample was characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The surface area of the Al-sorbent was determined by adsorption of methylene blue from aqueous solution. The results of FT-IR**,** XRD, TGA, DTA analyses of the Al-sorbent were in good agreement with literature data reported for boehmite type of aluminum oxyhydroxide [AlO(OH) or Al_2O_3. xH_2O, $1<x<1.5$)] with differing water content and crystalline size and have been reported [8]. In the current research only an FT-IR examination of the Al-sorbent was carried out. The FT-IR data are presented in Table 1 along with the previous data as well as literature data. The FT-IR spectra of the current sample are shown in Fig. 2a. and the FT-IR spectrum obtained from reference [8] are reproduced in Fig. 2b for comparison. As can

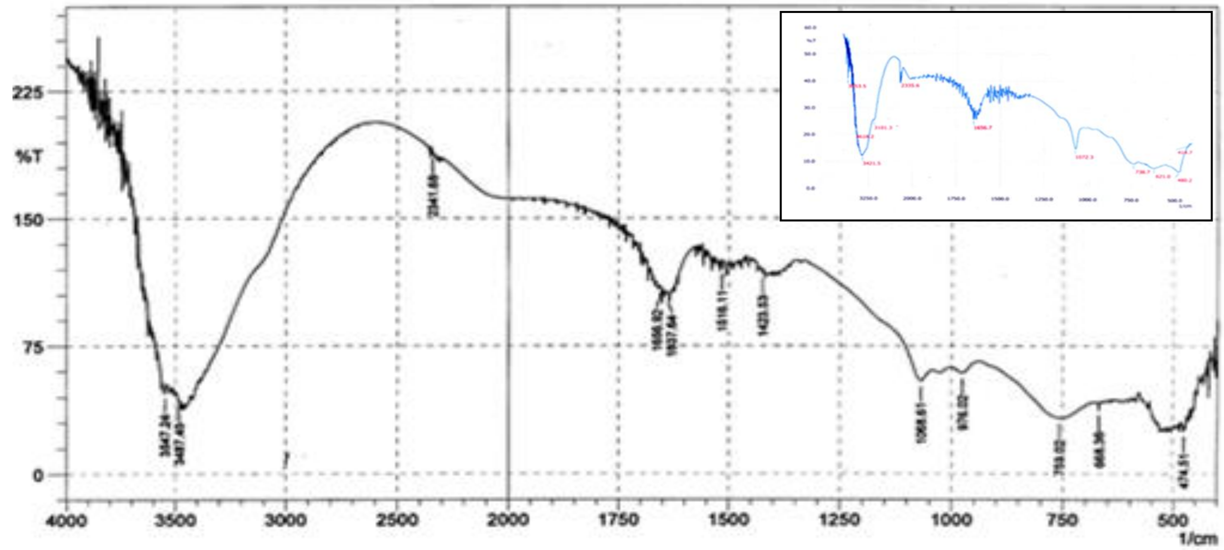

Fig. 2 FT-IR spectrum of freshly synthesized Al- Sorbent with inset of FT-IR spectrum of previous-generation Al- Sorbent [8]. beeen the presentFT-IR data are in good agreement with our previous

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Table 1. The FT-IR results along with reference data

Band Assignments	Al- Sorbent (cm^{-1}) (present experiment)	Al-Sorbent$^{\#}$ (cm^{-1})	Reference bands (cm^{-1})
Stretching vibration of Al-O	759	738.7	740 [9], 770-720[10]
Bending vibration of Al-O	474	414, 480	400[9]
Stretching vibration of O-H	1068	1072	1020 & 975 [10]
Vibrational mode of AlO_6	668.36	621	641 [13]
H-O-H bending of sorbed water	1657, 1638	1656	1640[13],1650 [11]
Bands due to surface O-H	3487, 3547	3421-3853	3700, 3740 & 3800[11], 3580-3700 [12]

3.1 Adsorption on Al- sorbent

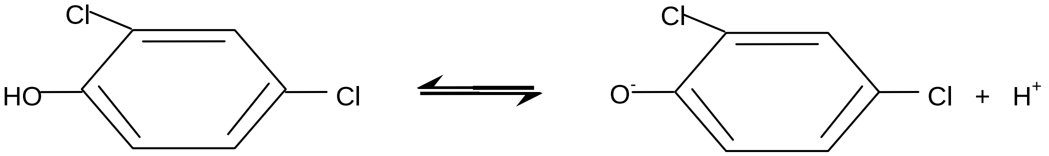
The maximum absorbance (**λ_{max}**) of 2,4-DCP was determined 285 nm in acidic medium, but in basic mediumtwo peaks were observed at 250 and 305 nm. The absorption peak observed at 250 nm varies in the range 247-252, but peak at 305 nm is near to visible range and did not change in basic region. So % removed of 2,4-DCP in basic medium was investigated at λ_{max} 305 nm. The molar absorption coefficient of 2,4-DCP was found at 285nm 0.0136 $Lmg^{-1}cm^{-1}$ and at 305 nm 0.0198 $Lmg^{-1}cm^{-1}$. The % of DCP removed by adsorption vs time are demonstrated in Figs 4 and the results are represented in Table 2.

Table 2. % of 2,4-DCP removed by adsorption on Al-sorbent at pH 5.85 and 11.92

Time / min	Percent removal of DCP (%)				
	pH 5.85			pH 11.92	
	30 ppm	40 ppm	80 ppm	40 ppm	80 ppm
10	-	-	-	1.54	2.95
20	1.13	1.11	1.45	3.0	3.38
30	1.60	2.22	3.38	3.95	5.36
40	2.23	3.15	4.11	4.55	6.34
50	3.02	3.71	4.93	5.99	6.90
60	3.94	4.09	5.56	6.82	7.28
70	4.16	4.83	5.66	7.17	7.34
80	4.63	5.03	5.85	6.94	7.30
90	4.38	5.21	6.02	-	-
100	4.38	5.03	6.11	-	-
110	4.38	5.41	6.11	-	-

It is observed that as the initial concentration of 2,4-DCP solution increases, the % removed also increases. It is clear that the amount of DCP adsorbed per gram of adsorbent increases with increasing initial concentration. This is due to increase in driving force of the concentration gradient with increasing initial adsorbate (2, 4- DCP) concentration.

The role of pH seems quite significant in case of adsorption, because the chemical properties of adsorbate molecules are greatly influenced by the pH of the medium. In dilute solution of 2,4-DCP the following equilibrium exists



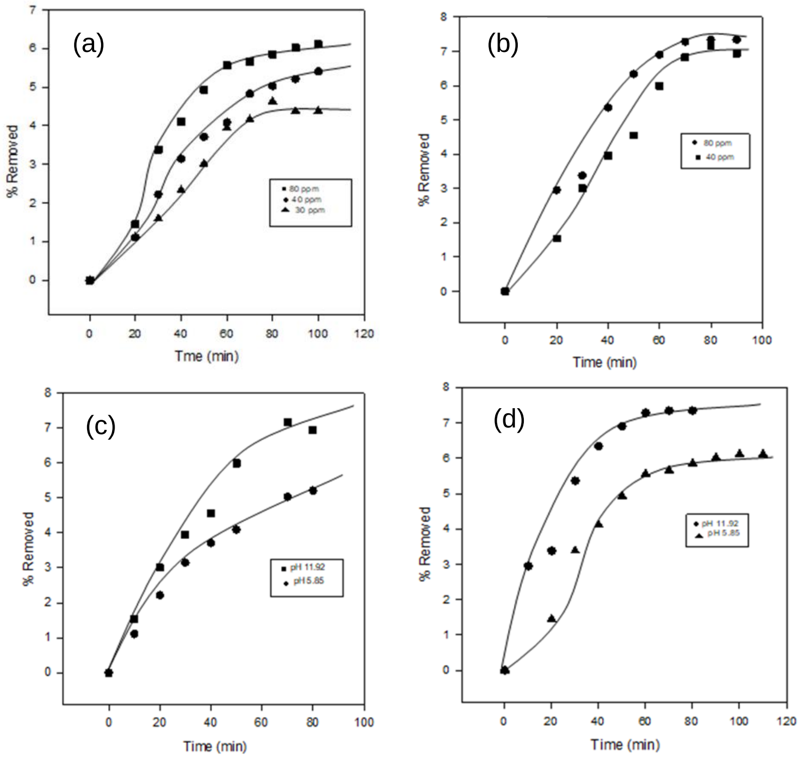


Fig. 3. % Removed vs Time for 2,4-DCP by adsorption on Al-Sorbent for different initial concentration at (a) pH 5.85, (b) pH 11.92 and% Removed vs Time for 2,4-DCP adsorbed on Al- sorbent at different pH (c)40 ppm, (d) 80 ppm.

The pKa of the above equilibrium at room temperature is 7.85. When the pH of the solution is lower than 7.85, 2,4-DCP mostly exists in the acidic form. It was observed that as the pH increased the % removed of 2,4-DCP is also increased . This is due to the fact that at higher pH the availability of phenolate ion is increased which can easily interact with Al-oxyhydroxide**.**

3.2 In-situ Electrocoagulation

In-situ electrocoagulation of 2,4- DCP was carried out at different initial concentration and pH of solution. The results are shown in Tables 3.and the corresponding plots of % of DCP removed vs time is given in Fig.4

Table 3. % of 2,4-DCP removed by in-situ EC using Al-electrode at pH 5.85 and 11.92

Time / min	Percent removal of DCP (%)				
	pH 5.85			pH 11.92	
	40 ppm	60 ppm	80 ppm	40 ppm	80 ppm
10	5.00	5.50	7.50	5.52	7.14
20	7.94	6.57	10.68	8.74	14.17
30	9.76	11.95	13.30	70.75	18.48
40	11.93	13.16	14.05	13.89	19.77
50	14.23	13.99	14.71	15.44	20.89
60	12.29	14.22	15.55	15.77	21.07
70	13.38	14.22	15.84	-	-

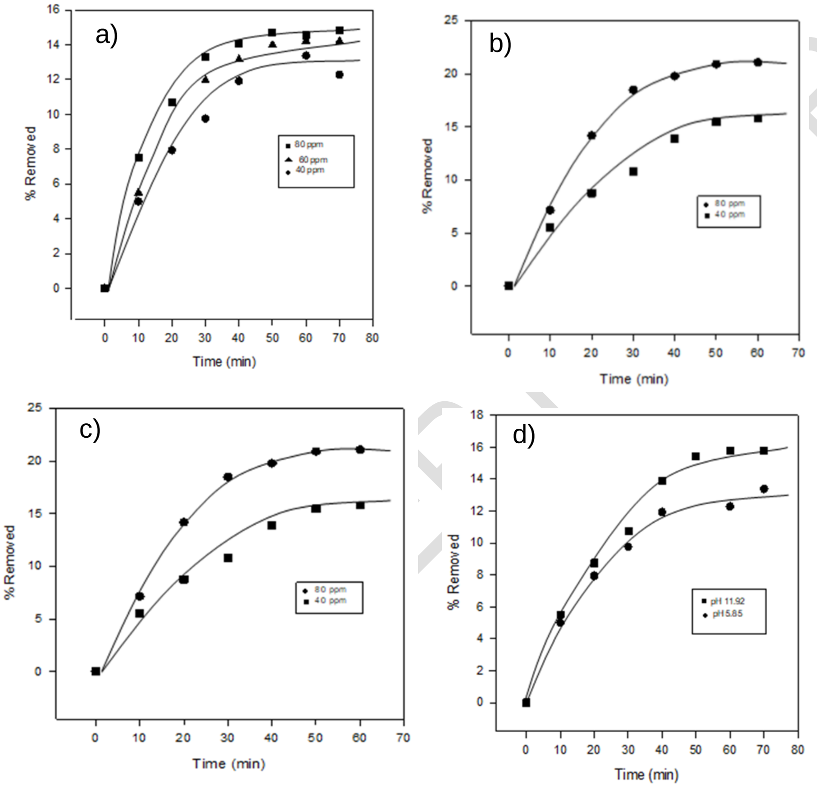


Fig. 4. % Removed vs Time for 2,4- DCP for different initial concentration at a) pH 5.85 b)11.92 and for different pH (c) 40 ppm, (d) 80 ppm by in-situ Electrocoagulation

3.2 Comparison of % Removed of 2,4- DCP by adsorption and in-situ Electrocoagulation

A comparison of the % of DCP removed by adsorption on electrochemically generated Al-sorbent and EC process is given in Table 4.

Table 4. Comparative results for the % DCP removed under different pH and different concentrations

Method	pH	Concentration (ppm)	% of DCP Removed
Adsorption	5.85	40	5.41
		80	6.11
	11.92	40	6.94
		80	7.34
In-situ electrocoagulation	5.85	40	13.38
		80	15.84
	11.92	40	15.77
		80	21.07

From the above table it can be concluded that in-situ electrocoagulation is more effective method than adsorption to remove 2,4- DCP from waste water. However, the percent of DCP removed is rather very low in both cases. The maximum of DCP removed in EC experiments under the present experimental conditions is about 21%.

3.2 TLC of extract

TLC examination of the extract shows a yellow-colored single spot (Rf = 0.71, in solvent 50% DCM in petroleum ether) for original compound and yellow-colored double spots (Rf value were 0.71 and 0.29 respectively in solvent 50% DCM in petroleum ether) for product compound. So, from TLC examination it is confirmed that a new compound (R_f = 0.29) was formed and the original compound was not completely destroyed. Again, the new compound was less polar than the original compound which was confirmed from R_f values. It thus indicates that the C –OH bond in phenolic group might have been involved in the reaction between the DCP and the adsorbent.

3.3 Molecular characterization of Aluminum oxyhydroxide and its interaction with 2,4-DCP

The molecular characterization of the electrochemically generated Aluminum oxyhydroxide and its interaction with 2,4-DCP were carried out by FT-IR analyses. The FT-IR spectrum of electrochemically generated Al oxyhydroxide is shown in Fig. 2a. The FT-IR spectrum of the precipitate collected after electrocoagulation of DCP using Al electrodes is shown in Fig. 5. The FT-IR spectrum of pure (untreated) 2,4-dichlorophenol is presented in Fig. 6. The FT-IR spectrum of the solid mass obtained after evaporating the solvent (Rotary evaporator) used for extraction of reaction product/products including the unreacted DCP is given in Fig. 7. The corresponding band positions along with reference data are presented in Tables 5 (Ref. Fig 2a. and 5) and Table 6 (Ref. Figs. 6 and 7).

***Table*5. The FT-IR results of Al- oxyhydroxide and its in-situ product with DCP**

Band Assignment	EC-generated Al-	EC-product with	Reference bands

	oxyhydroxides (cm^{-1})	2,4-DCP (cm^{-1})	(cm^{-1})
Stretching vibration of Al-O	759	720	738[8],740[9], 770-720 [9]
Bending vibration of Al-O	474.57	-----	480 and 414[8], 400[9]
Stretching vibration of O-H	1068.61	1066.68	1072[8], 1020 and 975[9]
Vibrational mode of AlO_6	668.36	668.36	621[8], 641[13]
H-O-H bending mode of sorbed water	1657, 1637.64	1617	1656[8], 1650[11]
Bands due to surface oxide	3487.45, 3547.24	3467.20, 3428.62, 3553.03	3421-3853[8], 3800[11], 3580-3700[12]
- C = C- (Ring stretch)	-------	1617.38	1600 – 1457[14]

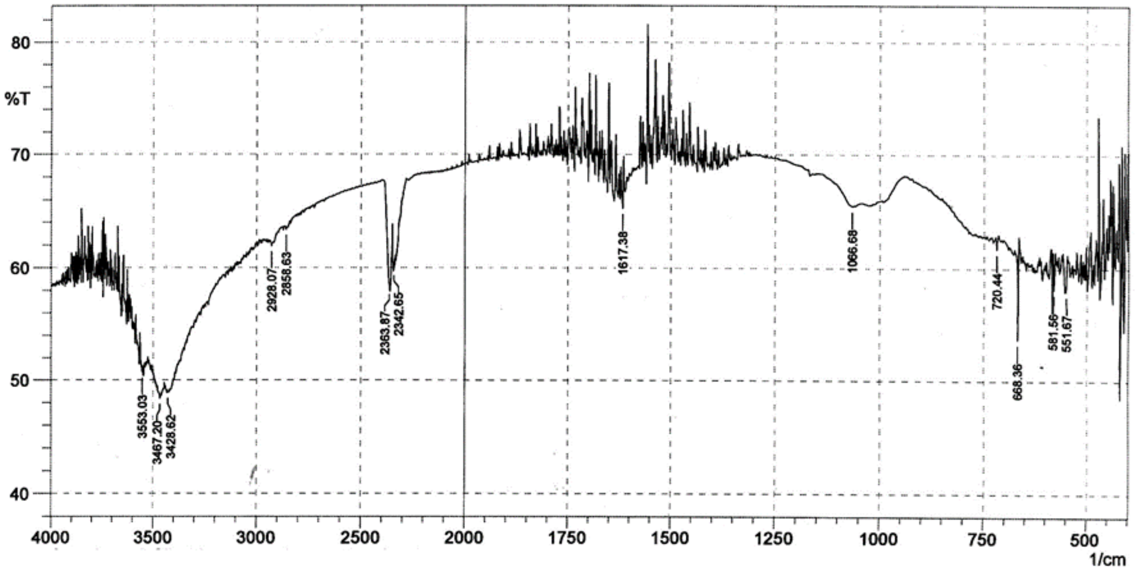


Fig.5. EC product with DCP

Close examination of the spectra presented in Fig.2a and 5 shows that after in-situ electrocoagulation of DCP, 2 new bands appear at 581.56 and 2928.00 cm^{-1} and the bands appearing at 759 and 1637.64 cm^{-1} in Al-oxyhydroxide have been shifted to 720.44 and 1617.38 cm^{-1} respectively in the EC-product with 2,4-DCP. This shifting of the two bands may be considered to be due to weakening of bonds as a result of chemical interaction between aluminum-oxyhydroxide and 2,4-DCP during electrocoagulation. This results thus indicate that the coagulation of 2,4-DCP and aluminum-oxyhydroxide is irreversible and 2,4-DCP chemically complexed with aluminum- oxyhydroxide.

The FT-IR spectrum of pure DCP is shown in Fig.6. It is clear that the FT-IR spectrum of DCP is quite complicated. It is rather difficult to assign all the bands. The prominent bands are recorded in Table 6. The FT-IR spectrum of the sample extracted after electrocoagulation of DCP is shown in Fig. 7.

Table 6. The FT-IR results of pure DCP and Extracted product

Bands assignment	DCP (cm^{-1})	Product band (cm^{-1})	Reference band (cm^{-1})
- O- H (phenol)	3655.26	3523.94	3650-3600[14]
C-Cl (Aryl chloride)	1053.18, 1093.69	------	1100-1053[14]
= C- H out of plane bending vibration	652.93, 724.30, 809.17, 859.32	------	900-690[14]

Substitution on the benzene ring (weak overtone bands)	1654.03	1696.47	2000-1667[14]
- C-O (Single bond stretching vibration of phenolic compound	1186.27, 1277.90	------	1220[14]
- C = C- (Ring stretch)	1478.50, 1583.63	1628.95	1600-1475[14]

Two new bands at 2367.72 and 2340.72 cm^{-1} appear in the spectrum of the product/products (Fig.7). Several weak bands appear in the region 757-1576 cm^{-1}. These bands are weak and it will be rather adventurous to make a conclusion based on this FT-IR spectra only.If, however, one considers the phenolic O–H band that appears at 3655 cm^{-1} in pure DCP sample, it becomes apparent that this band has been shifted to 3523.94 cm^{-1} – a shift of about 132 cm^{-1} unit in the lower field. This can happen only when the phenolic O-H bond is weakened by its interaction with Al-oxyhydroxide. From TLC analyses of the extracted fraction showed a new spot signifying a new compound in the mixture. We did not make any attempt to separate the product/products in the extracted solution. Therefore, it is not possible to identify the compound on the basis of present experimental data. Further investigation is needed to isolate the compound and analyses by FT- IR and NMR to conclusively identify the compound, and propose a mechanism of removal of DCP from the solution.

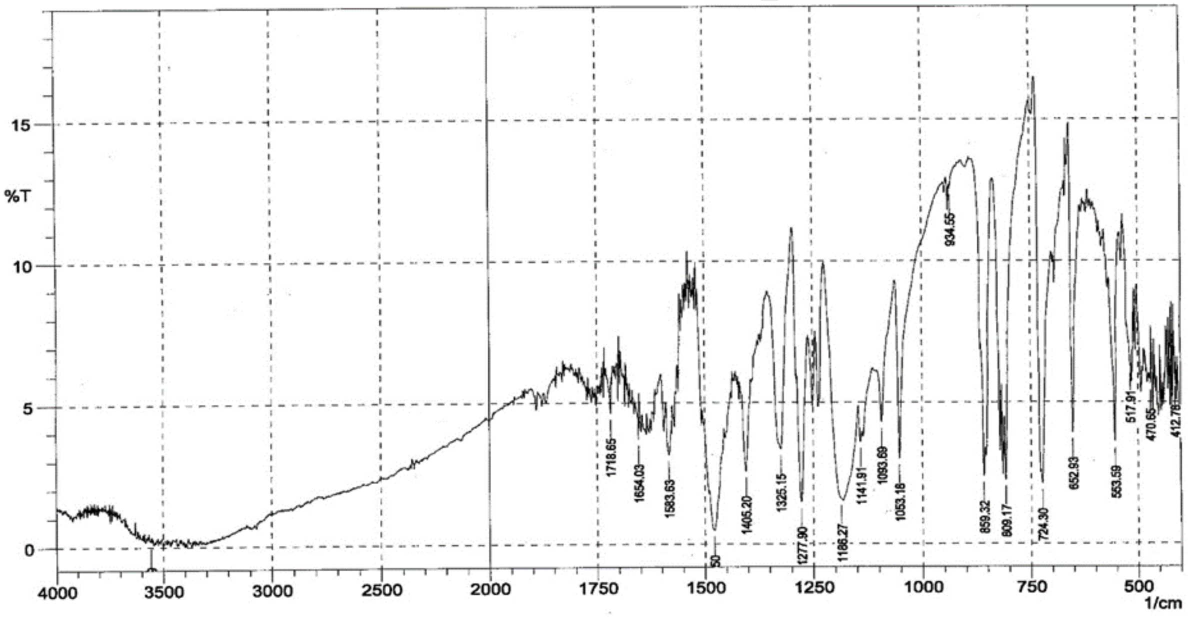


Fig6. FT-IR spectrum of2,4-DCP

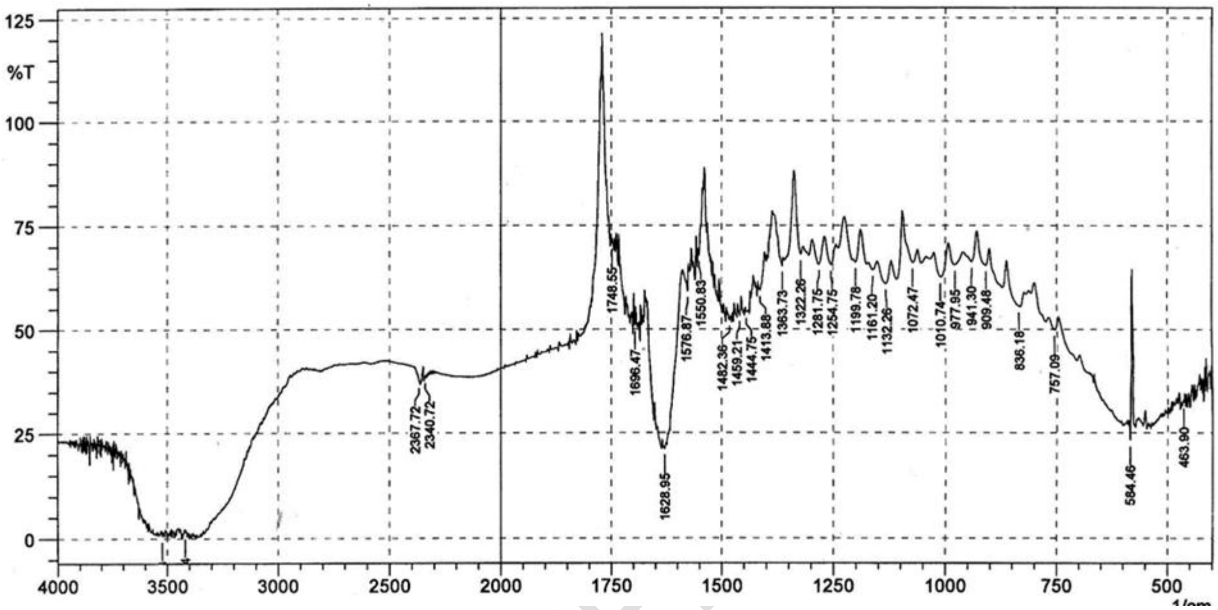


Fig.7. FT-IR spectrum of extracted product

4. CONCLUSION

Electrochemically generated aluminum oxyhydroxide was used to remove 2,4-DCP from waste water by in-situ electrocoagulation and by adsorption. The effect of initial concentration and pH was also investigated during removal of 2,4-DCP. It is found that percent of 2,4-DCP removed is more in basic medium, because in basic medium there is a prevalence of phenolate ion. It is also found from the experimental data that in-situ electrocoagulation is more effective method to remove 2,4- DCP than adsorption.

FUTURE STUDIES

During in-situ electrocoagulation a new compound was formed which was confirmed from TLC of the extracted solution after electrocoagulation. The new compound cannot be identified by FT-IR data, since this is for mixture of compound. Further investigation is needed to isolate the compound and analyze it by IR and NMR to characterize the compound and propose a mechanism of destruction of DCP under the present experimental conditions.

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APPENDIX

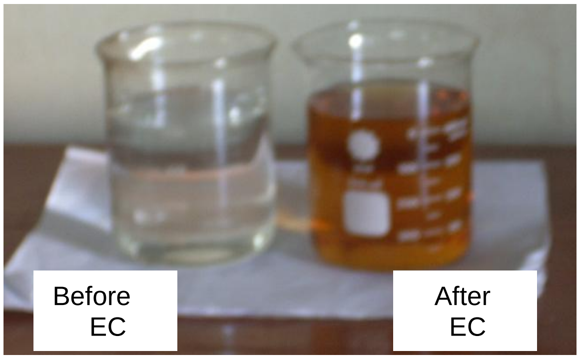

Fig. A1. Photograph of EC – Solution

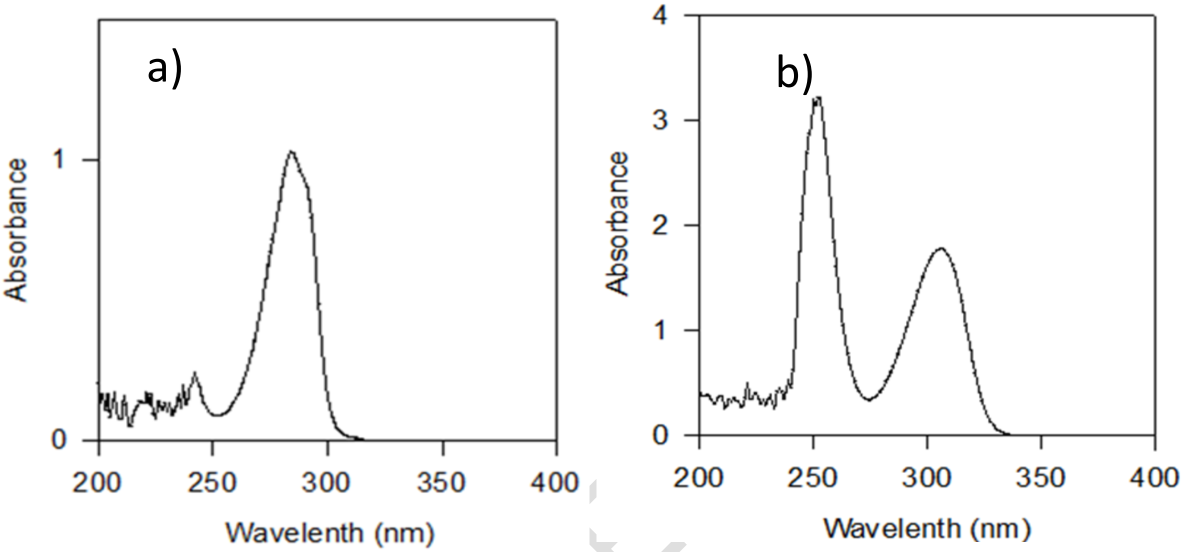

Fig. A2. Absorbance maxima of 2, 4- DCP (λ_{max}) at pH a) 5.85 and b) 11.92

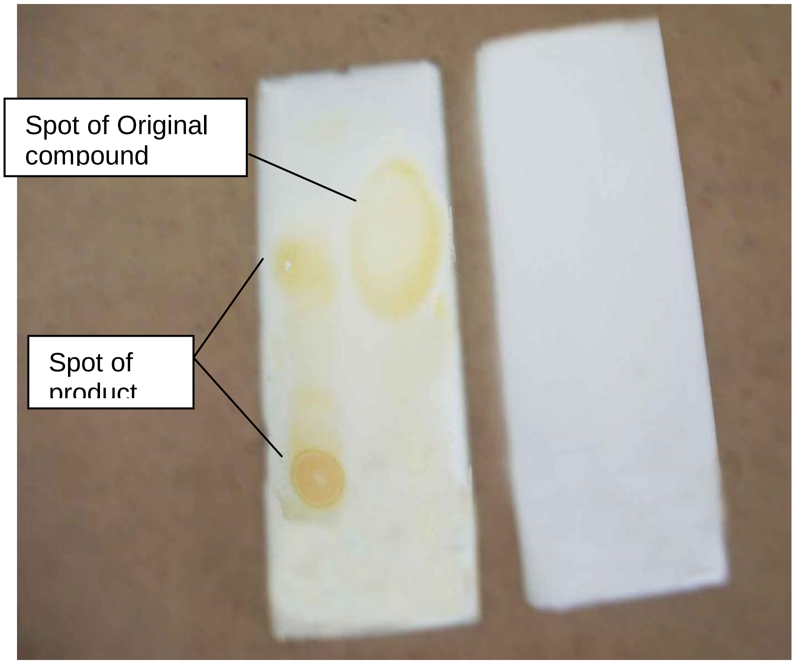

Fig. A3. Photograph of TLC- plate