



# Chlorinated breakdown products formed during oxidation of adsorbed phenol by electrochemical regeneration of a graphite intercalation compound



S.N. Hussain<sup>a,\*</sup>, H.M.A. Asghar<sup>a,1</sup>, H. Sattar<sup>c</sup>, N.W. Brown<sup>b</sup>, E.P.L. Roberts<sup>a,2</sup>

<sup>a</sup> School of Chemical Engineering and Analytical Science, University of Manchester, Manchester M13 9PL, United Kingdom

<sup>b</sup> Arvia Technology Ltd, The Innovation Centre, Sci-Tech Daresbury, Keckwick Lane, Daresbury WA4 4FS, Cheshire, United Kingdom

<sup>c</sup> Institute of Chemical Engineering & Technology, University of the Punjab, Lahore, Pakistan

## ARTICLE INFO

### Article history:

Received 31 October 2014

Received in revised form 23 May 2015

Accepted 30 May 2015

Available online 10 June 2015

### Keywords:

Chlorinated breakdown products

Phenol

Adsorption

Electrochemical regeneration

Graphite intercalation compound

## ABSTRACT

The process of adsorption using graphite intercalation compound (GIC) adsorbent with electrochemical regeneration has been investigated for the removal and oxidation of phenol in wastewater. The present study deals with the formation of chlorinated breakdown products released in treated water during electrochemical regeneration of GIC adsorbents. The main chlorinated breakdown products observed were 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol with lower concentrations of 2,4-dichlorophenol than 2-chlorophenol and 4-chlorophenol. Experiments performed at low current density ( $\leq 10 \text{ mA cm}^{-2}$ ), low initial phenol concentration ( $10 \text{ mg L}^{-1}$ ), and use of a chloride free catholyte minimised the concentration of chlorinated breakdown products. In addition, only a few  $\mu\text{g L}^{-1}$  of 2,4-dichlorophenol and 3,5-dichlorophenol were observed after five adsorption cycles operated in batch recycle mode for an initial phenol concentration of  $50 \text{ mg L}^{-1}$ . The formation of chlorinated breakdown products was found largely to be associated with the oxidation of phenol from solution as opposed to the adsorbed phenol. These results have important implications in reducing the formation of chlorinated breakdown products during wastewater treatment by adsorption and electrochemical regeneration.

© 2015 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## Introduction

A variety of separation processes have been developed for the removal of refractory pollutants from wastewater such as chemical treatment [1], electrochemical oxidation [2] and adsorption [3]. Adsorption is considered one of the significant methods in lieu of its simplicity for removing organic contaminants from water using activated carbon [4]. However, the economics and feasibility of the processes employing activated carbons for the treatment of wastewaters depends on the regeneration techniques. Several regeneration techniques such as thermal [5], chemical/solvent [6],

microbial [7], ultrasonic [8] and electrochemical regeneration [9] have been investigated. Minimal adsorbent losses, in situ regeneration and high regeneration efficiencies have made electrochemical regeneration to be an effective alternative to thermal regeneration [10]. However, long adsorption and regeneration times associated with high porosity and low electrical conductivity of activated carbon are the disadvantages of electrochemical regeneration [11,12]. In order to address these issues associated with the regeneration of activated carbon, a novel and innovative process has been developed at the University of Manchester [13]. This process requires a non-porous graphite intercalation compound (GIC) for the adsorption of low concentrations of organic contaminants present in wastewater followed by its electrochemical regeneration in a simple divided electrochemical cell. A wide range of organic species including pesticides, chlorinated compounds, dyes, oils and solvents have been shown to be effectively removed by this process [11,12,14]. The GIC adsorbent delivered a small adsorptive capacity for these pollutants, however, underwent quick adsorption and electrochemical regeneration in minutes. Extensive studies on the development of GIC adsorbents with improved adsorption characteristics have been reported elsewhere [15–17].

\* Corresponding author. Present address: Institute of Chemical Engineering & Technology, University of the Punjab, Lahore, Pakistan. Tel.: +92 3004239260.

E-mail addresses: [hussain\\_nadir@hotmail.com](mailto:hussain_nadir@hotmail.com) (S.N. Hussain), [edward.roberts@ucalgary.ca](mailto:edward.roberts@ucalgary.ca) (E.P.L. Roberts).

<sup>1</sup> Present address: Institute of Chemical Engineering & Technology, University of the Punjab, Lahore, Pakistan.

<sup>2</sup> Present address: Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB, Canada T2N 1N4. Tel.: +1 403 220 4466; fax: +1 403 284 4852.

In an electrochemical cell used for regeneration, each particle of GIC adsorbent behaves as an anode on which anodic oxidation of the adsorbed species takes place. Since, the regenerated adsorbent is transferred to the next adsorption cycle without additional treatment; the process does not generate secondary waste. However, partial oxidation of the adsorbed organics could generate various intermediate oxidation products causing contamination of the treated water. Electrochemical oxidation of organic contaminants in the presence of chlorides has been shown to generate highly toxic chlorinated organic intermediates [18].

Initially, it was assumed that the adsorbed organics are completely oxidised leaving no intermediate oxidation products in the treated water, or that these products remain adsorbed on the GIC during electrochemical regeneration [14]. However, recent studies carried out in batch and continuous electrochemical regeneration reactors have shown that intermediate oxidation products are formed during the electrochemical regeneration of phenol loaded GIC adsorbent. It was also found that oxidation of adsorbed phenol occurred in parallel with indirect (i.e phenolic oxidation from solution as opposed to the oxidation of sorbed phenolic) oxidation of phenol in solution [19]. In recent past, the effect of operating parameters including current density, pH of the solution, addition of electrolytes with phenol solution on the electrochemical regeneration of GIC has also been investigated [20]. In these studies, the formation of aromatic and aliphatic breakdown products has been reported. In addition, chlorinated breakdown products of phenol could also be formed due to indirect oxidation. Sodium chloride is often present in many industrial wastewaters and it is also a low cost, readily available electrolyte which can be added to reduce the cell potentials. Phenol can be chlorinated during electrochemical oxidation in the presence of chloride, leading to an increase in the toxicity and the environmental hazard associated with wastewaters [21]. In the process of adsorption and electrochemical regeneration, NaCl is often used as electrolyte in the cathode compartment of the electrochemical cell used for regeneration [11,12]. The present paper investigates the formation and the fate of chlorinated breakdown products released in solution during the treatment of water contaminated with phenol by adsorption and electrochemical regeneration of GIC adsorbent under a range of experimental conditions.

## Materials and methods

### Materials

Analytical grade phenol was supplied by Sigma Aldrich, UK. Analytical grades of other chemicals used in adsorption and calibration studies (including 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2-4 dichlorophenol, 2-5 dichlorophenol, 2-6 dichlorophenol, 3-5 dichlorophenol and 2,4,6-trichlorophenols) were also supplied by Sigma Aldrich, UK.

The adsorbent used was unexpanded flake GIC material, Nyex™ supplied by Arvia Technology Ltd, UK. This material is non-porous as indicated by Mercury porosimetry experiments and therefore does not possess any internal surface area. The Brunauer Emmett Teller (BET) surface area of the GIC adsorbent was determined by nitrogen adsorption and found to be  $1.0 \text{ m}^2 \text{ g}^{-1}$ . The mean particle diameter was found to be around  $480 \text{ }\mu\text{m}$  (range  $50\text{--}850 \text{ }\mu\text{m}$ ) as determined by laser diffraction (Mastersizer-2000, Malvern Instruments, UK).

### Methods

#### Adsorption studies

Adsorption isotherms were determined for mono-, di- and tri-chlorinated phenols by mixing a range of known concentrations of

100 mL of adsorbate solution with 20 g of adsorbent in 250 mL volumetric flasks. Mixing was carried out using a magnetic stirrer (ER LAUDA, Germany) at  $700 \text{ min}^{-1}$  for 30 min at room temperature. Previous kinetic studies showed that the time required to attain equilibrium for phenol and non-chlorinated oxidation products was found to be 30 min [19,20], and the same equilibrium time (30 min) was assumed to be applicable for the study of the adsorption isotherms of the chlorinated breakdown products. Initial and final samples were taken during each experiment and these were analysed as specified below. The adsorbent loading,  $q$  ( $\text{mg g}^{-1}$ ), was determined from the initial and final concentrations as:

$$q = \frac{(C_i - C_f)V}{m} \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final concentrations ( $\text{mg L}^{-1}$ ) of adsorbate,  $V$  is the volume (L) of solution and  $m$  is the mass (g) of adsorbent used.

In addition, competitive adsorption was also investigated for the chlorinated breakdown products by mixing a range of known masses of adsorbent with 100 mL of a solution containing mixture of 2-chlorophenol, 4-chlorophenol, 2-4-dichlorophenol and 2,4,6-trichlorophenol (each at a concentration of  $50 \text{ mg L}^{-1}$ ) for 30 min on a magnetic stirrer (ER LAUDA, Germany) at  $700 \text{ min}^{-1}$  at room temperature. Initial and final samples after adsorption were filtered using a  $0.45 \text{ }\mu\text{m}$  syringe filter and analysed as described in the Analysis section.

#### Sequential batch reactor

A sequential batch reactor (SBR) was used for carrying out the adsorption and electrochemical regeneration in the same device as shown in Fig. 1. This apparatus has been described elsewhere [20]. The anode current feeder (graphite Plate 5 mm thick) and the cathode (perforated 316 stainless steel plate with a thickness of 1 mm and 3 mm diameter perforations) were separated by a micro-porous Daramic 350 membrane. The area of each electrode was  $50 \text{ cm}^2$ , although some of the experiments were carried out in a slightly larger SBR having an electrode area of  $70 \text{ cm}^2$ , however, with the same geometry as that shown in Fig. 1. During adsorption, air was supplied through an array of orifices at the base of the cell to bring about the mixing of the adsorbent with the water.

#### Batch adsorption and electrochemical regeneration

For batch adsorption and electrochemical regeneration, a known mass of adsorbent was added to a measured volume of phenol solution of known concentration in the SBR and mixed for 30 min using air. After the completion of adsorption, the air supply was turned off and the adsorbent particles were allowed to settle for 2 min. The adsorbent settled into the anode compartment of the electrochemical cell at the base of the SBR to form a uniform bed of particles as shown in Fig. 1. Following settling of the adsorbent in the SBR, a sample of the supernatant water was collected and analysed as described below. No additional electrolyte was used in the anode compartment. However, on the cathode side, 400 mL of 0.3% NaCl solution (w/v) acidified with 5 M HCl (to pH,  $2 \pm 1$ ) (unless otherwise stated) was added as an electrolyte so that the catholyte was at the same level as the bed of settled adsorbent. After connecting the power supply to the anode and cathode of the electrochemical cell, a constant DC current was supplied for a fixed regeneration time so that the electrochemical regeneration of the adsorbent could take place. Current densities in the range of  $5\text{--}40 \text{ mA cm}^{-2}$  were used corresponding to an applied current of  $0.25\text{--}2.0 \text{ A}$ . The applied current was held constant for the duration of the regeneration time and the voltage across the electrochemical cell was monitored. After the completion of regeneration, the current was turned off and a sample of water was taken from the supernatant

Download English Version:

<https://daneshyari.com/en/article/227159>

Download Persian Version:

<https://daneshyari.com/article/227159>

[Daneshyari.com](https://daneshyari.com)