

Formation of Byproducts during Regeneration of Various Graphitic Adsorbents in a Batch Electrochemical Reactor

S. N. Hussain, H. M. A. Asghar, H. Sattar, N. W. Brown, and E. P. L. Roberts

Abstract—A water treatment technology employing the adsorption of dissolved organic contaminants from water and their electrochemical regeneration has been commercialized by Arvia Technology Ltd, UK. This technology focuses the adsorption of pollutants onto the surface of low surface area graphite based adsorbents followed by the anodic oxidation of adsorbed species in an electrochemical cell. However, some of the adsorbed species may lead to the formation of intermediate breakdown products due to incomplete oxidation. The information regarding the formation of breakdown products during electrochemical regeneration of these adsorbents is important for the effective application of this process to water treatment. In the present paper, the formation of the breakdown products during electrochemical regeneration of various graphite based adsorbents has been demonstrated.

Keywords—Arvia[®], Adsorption, Electrochemical Regeneration, Breakdown products.

I. INTRODUCTION

THE removal of organic pollutants from water by adsorption onto activated carbon is an effective and widely used method. However, the thermal regeneration of exhausted activated carbon is a costly process. Electrochemical regeneration of activated carbon is being considered as an effective process with regeneration efficiencies above 90% [1]. In addition, on-site removal and destruction of the organic pollutants can be achieved during electrochemical regeneration of the adsorbent. However, the electrochemical processes used for water treatment have certain disadvantages including high operating costs associated with high cell voltages due to relatively low electrical conductivity of the water to be treated. Moreover, the formation of toxic byproducts particularly chlorinated species cannot be avoided. In order to address the issues associated with the electrochemical treatments, an innovative and state of the art process was developed at University of the Manchester. This process exploits graphite based adsorbents for the adsorption of low amounts of impurities present in water followed by the anodic oxidation of adsorbed species in a simple electrochemical cell. The graphitic adsorbent is non-porous and therefore possesses very low adsorptive capacity as compared to activated carbon, but it is capable of giving quick adsorption. The other unique and most important

property of this adsorbent is its high electrical conductivity which has made it a suitable material to be exploited for commercial electrochemical regeneration process. The process of exploiting such an adsorbent for adsorption and electrochemical regeneration in treating the low concentrations of organics in water is termed as Arvia[®] process. The process can be operated in batch as well as in continuous mode.

The Arvia[®] process has the ability to reduce the costs because the mass transfer process occurs during the adsorption stage and the graphite based adsorbent due to its high electrical conductivity offers low cell voltages. Ideally, the adsorbed impurities from the surface of the adsorbent should be oxidized completely into carbon dioxide and water. However, the formation of some of the intermediate breakdown products is possible depending upon the regeneration conditions. The studies have shown that breakdown products are generated during the electrochemical regeneration of a graphite intercalation compound adsorbent onto which phenol was adsorbed [2], [3]. The major intermediate products including aromatic (benzoquinone, hydroquinone, catechol) and aliphatic (maleic and oxalic acid) species have been reported [2], [3]. It has also been shown that these intermediates were formed at lesser concentrations in comparison to the concentration of initial stock solution of phenol [2]. A most recent study has also shown that these intermediate products can be formed either by the oxidation of adsorbed species or by indirect oxidation of organics in solution [3]. The effect of a range of operating parameters including current density, pH, electrolyte and initial concentration of the contaminant on the formation of breakdown products have shown that the indirect electrochemical oxidation of organics in solution is the main mechanism responsible for the formation of breakdown products. However, it was also suggested that the use of high capacity adsorbents will further authenticate this phenomenon. In the present study, three adsorbents including graphite intercalation compound-bisulphate (GIC-bisulphate), recycled vein graphite (RVG) and expanded graphite (EG) were investigated for the formation of intermediate oxidation products in an air agitated sequential batch reactor. Phenol was selected as a sample pollutant for its adsorption onto these adsorbents followed by their electrochemical regeneration. The adsorption characteristics of RVG and EG have already been reported [4], [5]. However, the investigation of the

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breakdown products during electrochemical regeneration of RVG and EG has not been investigated before.

II. MATERIALS AND METHODS

A. Materials

The adsorbent materials, GIC-bisulphate, RVG and EG were provided by Arvia Technology Ltd UK and were used in the experiments without any treatment. These materials were characterized using Laser size analyser, nitrogen adsorption, bulk density, SEM, bed electrical conductivity. The characteristics of these materials are provided in Table I.

TABLE I
CHARACTERIZATION OF GIC-BISULPHATE, RVG AND EXFOLIATED GRAPHITE

Adsorbent	Particle size (μm)	BET surface area (m^2/g)	Bulk density (g/cm^3)	Bed electrical conductivity (S/cm^{-1})	Particle morphology
GIC-bisulphate	484	1	0.896	0.8	Flakes
RVG	436	1.54	0.96	1.4	Grains
Exfoliated Graphite	784	17	0.225	1.6	Flakes

In wastewater treatment, phenol has been widely used as a model pollutant because it represents a number of compounds that are considered toxic species causing water pollution [6]. Therefore, phenol was chosen as a model contaminant for the present study.

Analytical grades of all the chemicals including phenol, benzoquinone, hydroquinone, catechol, sodium chloride, hydrochloric acid etc were supplied by Sigma-Aldrich[®], UK.

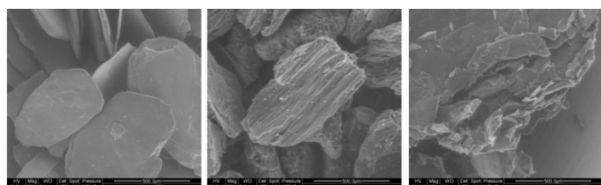


Fig. 1 SEM images of GIC-bisulphate (left), RVG (middle) and EG (right)

B. Batch Electrochemical Reactor

The batch electrochemical cell shown in Fig. 2 is used for carrying out the adsorption and electrochemical regeneration. It is a simple Y-shaped air agitated sequential batch electrochemical cell. The details of the electrochemical reactor have been described elsewhere [3].

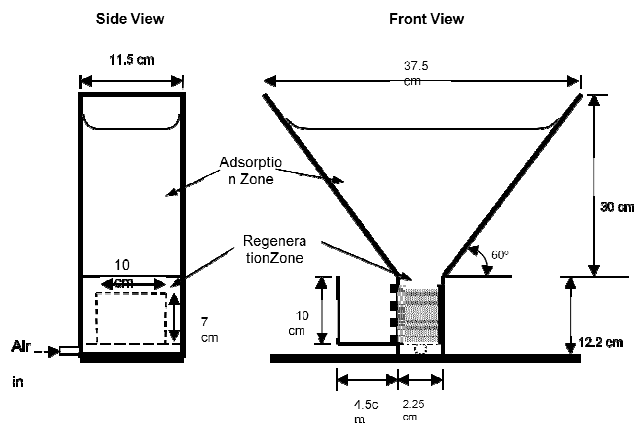


Fig. 2 Schematic diagram of the batch electrochemical reactor used for adsorption and electrochemical regeneration studies [3]

C. Methods

A 500mL of 100 mg L⁻¹ of phenol solution was mixed with a fixed quantity of adsorbent in the batch electrochemical reactor, as shown in Fig. 2, for 30min. On the completion of adsorption, the air supply was turned off and the adsorbent particles were allowed to settle into the anodic section of the electrochemical reactor to form a uniform bed of particles. The settled particulate bed was in contact with the graphite anode plate that in turn was separated from the perforated steel cathode plate by a polymer membrane. Afterwards, a sample of the water present above the settled adsorbent was taken from the reactor and was analyzed as specified in the following section. Electrochemical regeneration of the settled adsorbent bed was performed at 0.5 A for 20min (10mA cm⁻²) unless otherwise specified. The catholyte was composed of 0.3% NaCl aqueous solution acidified with HCl and the pH of the catholyte was kept below 2. After the completion of the regeneration, the water was removed from the reactor. A sample of this water was also analyzed using the method as described in the following section. Phenol solution of the same concentration and same volume was added into the electrochemical reactor for second adsorption and then afterwards second regeneration. In this way, five adsorptions and five regenerations were performed. The whole experiment was carried out for GIC-bisulphate, RVG and EG.

D. Analysis

HPLC (Varian Prostar) was done to analyze the aqueous samples collected after adsorption and electrochemical regeneration. A UV detector was used in conjunction with HPLC. The column used a C18 stationary phase supplied by Phenomenex. The mobile was composed of 50% methanol solution in ultrapure water at a flow rate of 0.7 mL min⁻¹. The UV detector was used with a wavelength of 210nm.

III. RESULTS AND DISCUSSIONS

Benzoquinone, catechol, hydroquinone, maleic and oxalic acid were seen as the main breakdown products resulted due to electrochemical regeneration of graphitic adsorbent [2], [3]. Among these oxidation products the rate of degradation of

benzoquinone was observed lower compared to its formation rate [2]. Therefore, in the present study only the trend of formation of benzoquinone during adsorption and regeneration cycles for the three adsorbents; GIC-bisulphate, RVG and EG have been shown in Figs. 3 and 4. Relatively higher concentrations of breakdown products (in terms of benzoquinone) were observed as a result of electrochemical regeneration of phenol loaded GIC-bisulphate. In case of RVG, no significant variation in the formation of the breakdown products was observed as shown in Figs. 3 and 4. However, RVG has relatively higher specific surface area and electrical conductivity (See Table I). Expanded graphite has the highest specific surface area in comparison to GIC-bisulphate and RVG. The high surface area of EG can be justified due to its rough surface morphology as evident in Fig. 1. It is likely that more quantity of phenol was adsorbed per unit mass of the EG adsorbent. Previous studies have shown clearly that there are two mechanisms responsible for the oxidation of adsorbed species. One is the oxidation of adsorbed species at the surface of the graphitic adsorbent and the other is the indirect oxidation of organics present in solution. It was also seen that the main factor responsible for the formation of breakdown products was due to the indirect oxidation in solution [3]. It was also speculated that the use of relatively high capacity adsorbents will minimize the formation of intermediate breakdown products. The higher quantity of phenol was adsorbed onto expanded graphite owing to its maximum surface area (See Table I) leaving lesser amounts of the phenol in solution (data not shown). However, under the conditions of experiments, lesser quantities of breakdown products were observed during regeneration of EG compared to the breakdown products formed in the case of GIC-bisulphate and RVG. This shows that almost complete mineralization of the adsorbed phenol took place with negligible amount of indirect oxidation in solution leading to the formation of much lesser quantities of the breakdown products. Thus, it can be concluded that the expanded graphite adsorbent can be effectively used for the commercial application of this technology due to the formation of minimum amounts of breakdown products.

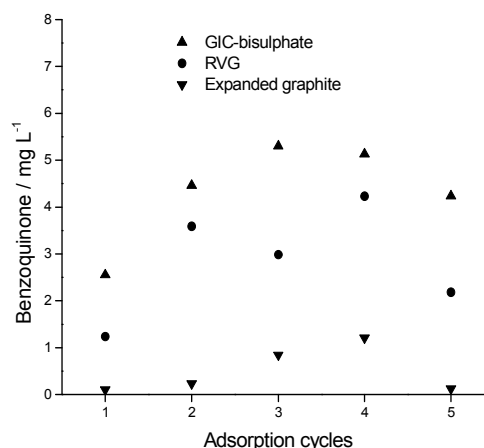


Fig. 3 Formation of benzoquinone in solution after a series of adsorption cycles; Regeneration conditions for GIC-bisulphate and RVG: 0.5mA current was passed through 10mm deep bed for 20min at a current density of 10mA cm⁻²; Regeneration conditions for expanded graphite: 0.5mA current was passed through 10mm deep bed for 40min at a current density of 10mA cm⁻²

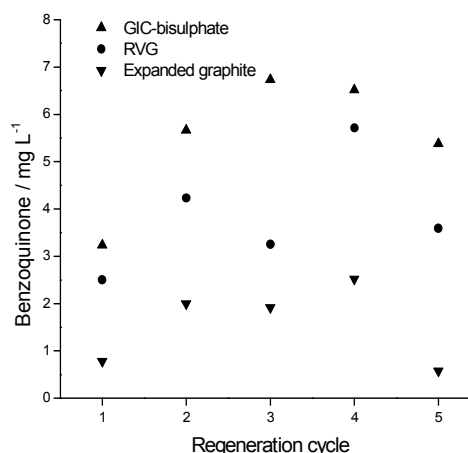


Fig. 4 Formation of benzoquinone in solution after a series of regeneration cycles; Regeneration conditions for GIC-bisulphate and RVG: 0.5mA current was passed through 10mm deep bed for 20min at a current density of 10mA cm⁻²; Regeneration conditions for expanded graphite: 0.5mA current was passed through 10mm deep bed for 40min at a current density of 10mA cm⁻²

IV. CONCLUSIONS

The present study has shown that less amounts of the breakdown products (in terms of benzoquinone) were resulted due to electrochemical regeneration of phenol loaded expanded graphite in comparison to GIC-bisulphate and RVG. This shows that the use of high capacity adsorbents with high electrical conductivity can be effectively regenerated in a simple electrochemical reactor. This further shows that the adsorbed species onto the surface of these adsorbents are completely mineralized to carbon dioxide and water leaving no objectionable intermediate products. Thus, the present investigation has important implications regarding the commercial application of adsorption using graphitic

adsorbents and their electrochemical regeneration for wastewater treatment.

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