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The effects of anodic treatment on the surface chemistry of a Graphite Intercalation Compound

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ABSTRACT

Graphite intercalation compounds (GIC) can be used as adsorbents for the removal of dissolved organic contaminants in water, and can be rapidly regenerated by electrochemical treatment. After electrochemical regeneration, the adsorption capacity of the GIC is often observed to increase compared to fresh adsorbent. This increase has been attributed to roughening of the surface as well as changes in surface chemistry. Specific surface areas of fresh and electrochemically treated GICs have been measured, and show no significant variation. Consequently, the electrochemical anodic oxidation process used to regenerate the material has been investigated, and these changes, specifically the transformation of the oxygen containing functional groups which is believed to give the GIC its surface chemistry properties, has been measured and studied. Analytical techniques including Scanning Electron Microscopy, Attenuated Total Reflectance Fourier Transform Infra-red spectroscopy, X-ray Photoelectron spectroscopy, Energy Dispersive X-ray spectroscopy and Boehm titrations were used to detect and estimate the relative amounts of functionalities such as carboxylic, quinone and lactonic functional groups. Results showed that fresh GICs have acidic quinone and carboxyl groups on the surface. These functional groups increase upon regeneration, however sustained regeneration leads to the formation of basic lactones which offset the relative amounts of the acidic groups. Acidic functional groups have been reported to increase adsorption, and consequently, there is an initial increase in adsorption due to surface acidic functionalities. Subsequent regeneration leads to the formation of basic functional groups which limit this enhanced adsorption.

1. Introduction

Adsorption has become one of the most favoured technologies for wastewater treatment, and significant research is on-going to find an alternative to the more conventional granular activated carbon (GAC) adsorption systems [1,2]. One alternative that has been studied is the combination of a continuous adsorption and electrochemical regeneration process using a non-porous, electrically conductive graphite intercalation compound (GIC) adsorbent. Although this material has significantly less surface area (approximately 1 $m^2\,g^{-1}$) than activated carbon (which has surface areas of 600–1200 $m^2\,g^{-1}$), it promises a more environmentally and economically feasible option to activated carbon systems because GICs can be regenerated in-situ every hour, so its surface area is available again, unlike GAC which is usually used only once before being removed for off-site regeneration. It has been calculated that over an 18-day operation, there is more surface area available for adsorption with GIC than GAC [3]. The non-porous nature of the GIC adsorbent ensures rapid kinetics, with adsorption equilibrium reached in about 45 minutes due to the lack of diffusion into pores which is the rate limiting factor for porous activated carbon.

GICs are a type of modified graphite compounds that have molecules intercalated between the graphene sheets in the graphite lattice. These intercalates, which could be cationic or anionic generally, impart new or enhance already existing properties such as catalysis, electrical conductivity and adsorptive properties [4,5]. Surface chemistry has a significant impact on adsorption [6,7] and it is well documented that electrochemical treatment can affect surface chemistry [8]. The GIC used in this work shall be referred to its tradename, Nyex^{TM}.

Adsorption capacity of this particular GIC has been observed to initially increase with electrochemical regeneration, before decreasing, and this work aims to explain how this is affected by changes in adsorbent surface functionality. Possible explanations for this include the generation of more surface area due to material degradation (which exposes more surfaces), and/or formation

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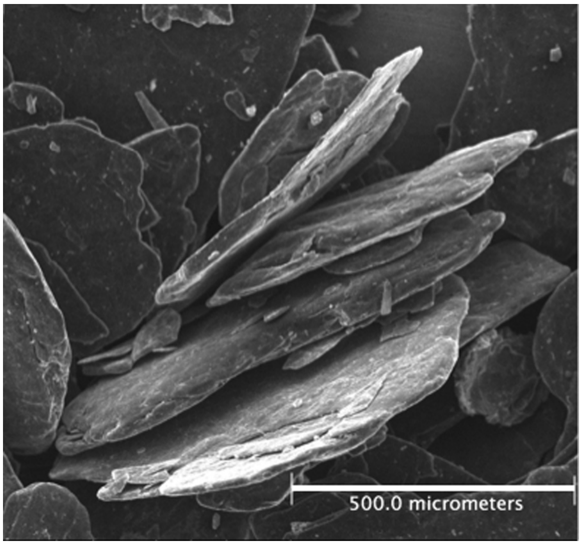


Fig. 1. SEM image of the GIC adsorbent used in this study, Nyex^{TM} 1000.

of more active sites due to the decomposition of acidic oxygen containing functional groups (OCFG). Many authors have reported the decomposition of acidic oxygen containing functional groups as one key mechanism for the formation of new active sites along the edges of graphene due to unshared electron pairs [9,10]. It is also widely acknowledged that adsorption of organic molecules, especially those with functional groups, is strongly affected by the the adsorbent's surface chemistry [11,12]. This work tests this hypothesis, and explores the relationship between changes in surface chemistry of electrochemically oxidised GICs and the enhanced adsorptive performance for the removal of organic contaminants.

2. Experimental Procedure

2.1. Materials

The GIC used in this work was GIC-bisulphate, and was supplied by Arvia Technology Ltd, UK as Nyex^{TM} 1000, a non-porous laboratory grade material with no internal surface area (confirmed by a combination of mercury porosimetry, helium pycnometry and nitrogen adsorption techniques). A GIC was used in this work because the higher charge carrier intercalates offer increased electrical conductivity. It has a mean particle size of 500 microns, particle density of 2.2 g cm^{-3}, a measured surface area of 1.2 m^2 g^{-1}, and is of flake morphology. A dry packed bed of this material was found to have a conductivity of 0.8 S cm^{-1}. Specific surface areas were measured using Tristar 3000 Surface Analyser by Micromeritics. An SEM image of the GIC, showing its flake morphology, is shown in Fig. 1. The catholyte used for the electrochemical regeneration was a slightly acidified 0.3% w/w sodium chloride solution made from analytical grades of hydrochloric acid (37% concentration) and sodium chloride granules (99% purity) supplied by Sigma Aldrich UK. The catholyte was acidified to pH of 1.2 by addition of small amount of HCl to protect the membrane used in the cell. The adsorbate used in the formulation of the synthetic wastewater was Acid Violet 17 (AV-17) which is used as a model compound organic compound for testing the adsorption and electrochemical regeneration performance of this process [13]. It was supplied as a dye containing 22 wt% AV-17.

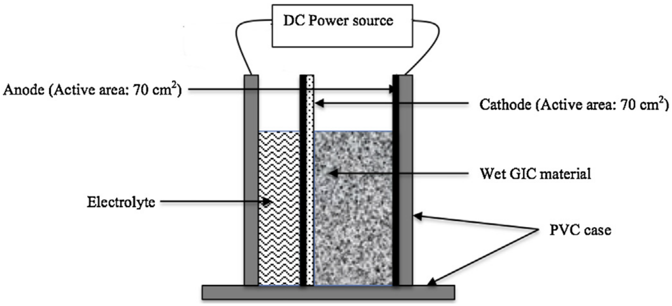
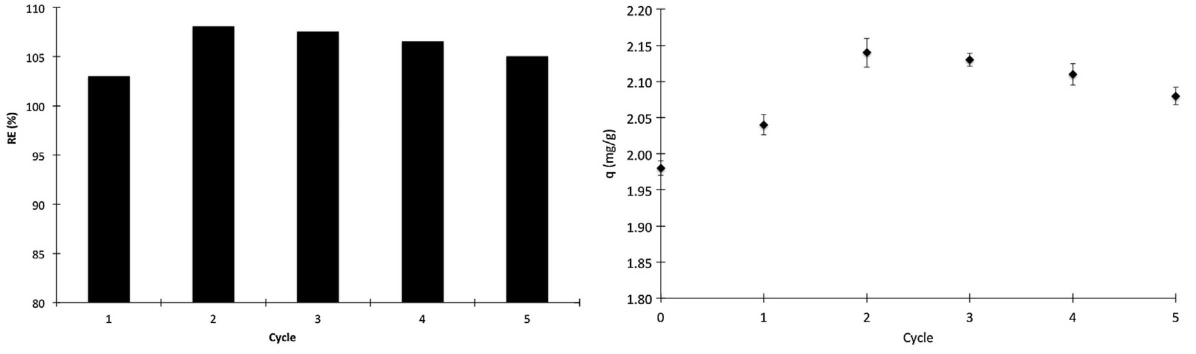


Fig. 2. Schematics of the electrochemical cell with loaded GIC during the electrochemical oxidative treatment.

2.2. Methodology

Techniques used to measure the surface functional groups of the GIC include Energy Dispersive X-ray (EDX) spectroscopy, Attenuated Total Reflectance Fourier Transform Infra-red (ATR-FTIR) spectroscopy and X-ray Photoelectron spectroscopy (XPS). Temperature programmed desorption (TPD) which is used extensively to investigate and measure such functionalities on the surface of most adsorbents could not be used because the GIC would exfoliate at the temperatures at which TPD analyses are carried out.

Four samples of different durations of electrochemical treatments were investigated: fresh GIC and GIC treated electrochemically for 30, 45 and 90 minutes at a current density of 14 mA cm^{-2} which had been shown to be optimal for regeneration [14]. The GIC, mixed with deionised water to keep the bed moist (50% w/w), was loaded into the anodic chamber of the electrochemical cell. No electrolyte was added to the bed although it is possible for ions



(a) Regeneraion Efficiency

(b) Equilibrium loading of AV-17

Fig. 3. (a)Showing how the regeneration efficiency of the GIC adsorbent varies with regeneration cycles. Regeneration efficiencies are calculated as a ratio of the loading after regeneration to the initial loading (at cycle 0), and (b) the variation of Acid Violet 17 dye loading on the adsorbent as equilibrium with regeneration cycles. Experimental conditions: 1 litre of 100 ppm AV-17 solution; mass of adsorbent = 20 g, current of 1.0 Amp (14 mA cm^{-2}) and mean cell voltage across all five cycles = 8.38 +/- 1.23 V.