

# Adsorption and Electrochemical Regeneration for Industrial Wastewater Treatment

H. M. Mohammad, A. Martin, N. Brown, N. Hodson, P. Hill, E. Roberts

**Abstract**—Graphite intercalation compound (GIC) has been demonstrated to be a useful, low capacity and rapid adsorbent for the removal of organic micropollutants from water. The high electrical conductivity and low capacity of the material lends itself to electrochemical regeneration. Following electrochemical regeneration, equilibrium loading under similar conditions is reported to exceed that achieved by the fresh adsorbent. This behavior is reported in terms of the regeneration efficiency being greater than 100%. In this work, surface analysis techniques are employed to investigate the material in three states: 'Fresh', 'Loaded' and 'Regenerated'. 'Fresh' GIC is shown to exhibit a hydrogen and oxygen rich surface layer approximately 150 nm thick. 'Loaded' GIC shows a similar but slightly thicker surface layer (approximately 370 nm thick) and significant enhancement in the hydrogen and oxygen abundance extending beyond 600 nm from the surface. 'Regenerated' GIC shows an oxygen rich layer, slightly thicker than the fresh case at approximately 220 nm while showing a very much lower hydrogen enrichment at the surface. Results demonstrate that while the electrochemical regeneration effectively removes the phenol model pollutant, it also oxidizes the exposed carbon surface. These results may have a significant impact on the estimation of adsorbent life.

**Keywords**—Graphite, adsorbent, electrochemical, regeneration, phenol.

## I. INTRODUCTION

INDUSTRIAL effluents contain considerable amounts of microorganisms that vary corresponding to the scope of work of each factory. The evaluation of industrial wastewater is based on several parameters such as pollutant concentration, biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS), and total dissolved solids (TDS). However, the quality of industrial effluent is questioned to meet Environmental Protection Agency (EPA) standards before reuse or discharge to natural waters to prevent threats to aquatic creatures and the natural environment. Due to variant microorganism loads that occur in these industrial wastewaters, alternative treatment methods rather than conventional processes are needed to make reuse viable. In the wastewater treatment sector, treatment technologies that have been investigated include: ozonation, catalytic ozonation, chemical oxidation, and adsorption with regeneration (thermal, extraction, surfactant,

reaction, catalytic and electrochemical) [1]-[3]. In order to form comparisons, review of the literature shows that adsorption with electrochemical regeneration is an economic treatment method offering benefits including short treatment time, low cost, low energy, minimal chemical addition, adsorbent regeneration, no wastes (except gases), complete on-site treatment and flexibility of operational parameters [4]. In addition, the advantage of electrochemical regeneration is that it is free of generating secondary effluent. However, several questions have been raised concerning electrochemical regeneration, including whether the treatment was conducted directly on the adsorbent surface when passing electrical current, oxidation occurred indirectly via adsorbent active sites, or chemicals were oxidized in the bulk liquid [5]. Therefore, deep investigation into the process of adsorption and electrochemical regeneration process would clearly enhance our understanding of the treatment mechanisms.

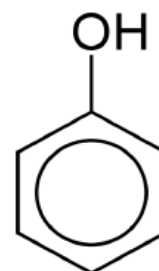


Fig. 1 Molecular structure of Phenol

## II. MATERIAL AND METHODS

Phenol, molecular structure shown in Fig. 1, ( $\geq 99\%$ ) pure was purchased from Sigma Aldrich, UK. A 200 mg/L stock phenol solution was prepared and diluted to 20, 40, 60, 80, 100, and 150 mg/L. Hydrochloric acid (HCl; 37%) ACS reagent and sodium hydroxide ( $\geq 97\%$ ) pellets were purchased from Sigma Aldrich and used to adjust the pH to the desired level. Sodium chloride was purchased from Sigma Aldrich and used to prepare all electrolyte solutions used herein. Concentrations of 0.1%, 0.3%, and 0.6% by weight were prepared and acidified with 5 mL of HCl to reach a pH of 1.5–1.7. Nyex1000, a patented electrically conducting graphite sulfur intercalation-based adsorbent produced by Arvia Technology Ltd., was used as the adsorbent herein. The particle diameter of Nyex1000 was measured, sieved and allocated within the range of 100–700  $\mu\text{m}$  as received. Nitrogen adsorption revealed the surface area of Nyex1000 to be 1  $\text{m}^2/\text{g}$ , which is very small in relation to activate carbon,

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known to have a surface area of up to 2000 m<sup>2</sup>/g. For each experiment, a specified amount of Nyex1000 was poured in a 250 mL beaker and mixed with 5–10 mL deionized water to prepare a paste.

The mini-SBR, referred to as the Y-cell, was used to perform part of the experiments in this study. The SBR consisted of anodic and cathodic compartments separated by a micro porous Daramic 350 membrane with 400 micron thickness and 58% permeability. The anode electrode was

made of a 5 mm thick graphite plate placed within the electrochemical regeneration zone as the electrical current provider. The cathode electrode was a 1 mm thick 316 stainless steel plate placed toward the catholyte aquatic bulk. Both electrodes were designed to provide an area of 70 cm<sup>2</sup> each for the regeneration zone inside the anodic compartment. The anodic compartment has a volume of 7,115 cm<sup>3</sup>, which can hold up to 7 L of solution. However, 1 L was the fixed volume used in all adsorption experiments.

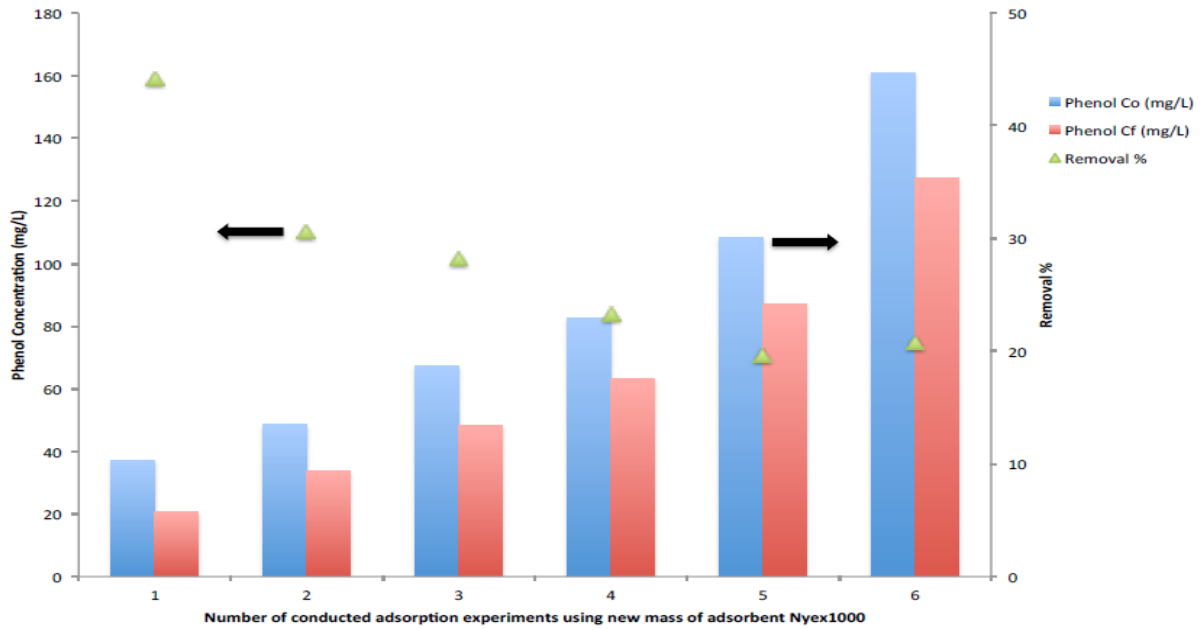


Fig. 2 Effect of phenol initial concentration (Nyex1000 mass = 100 g, time = 60 min, v = 1L)

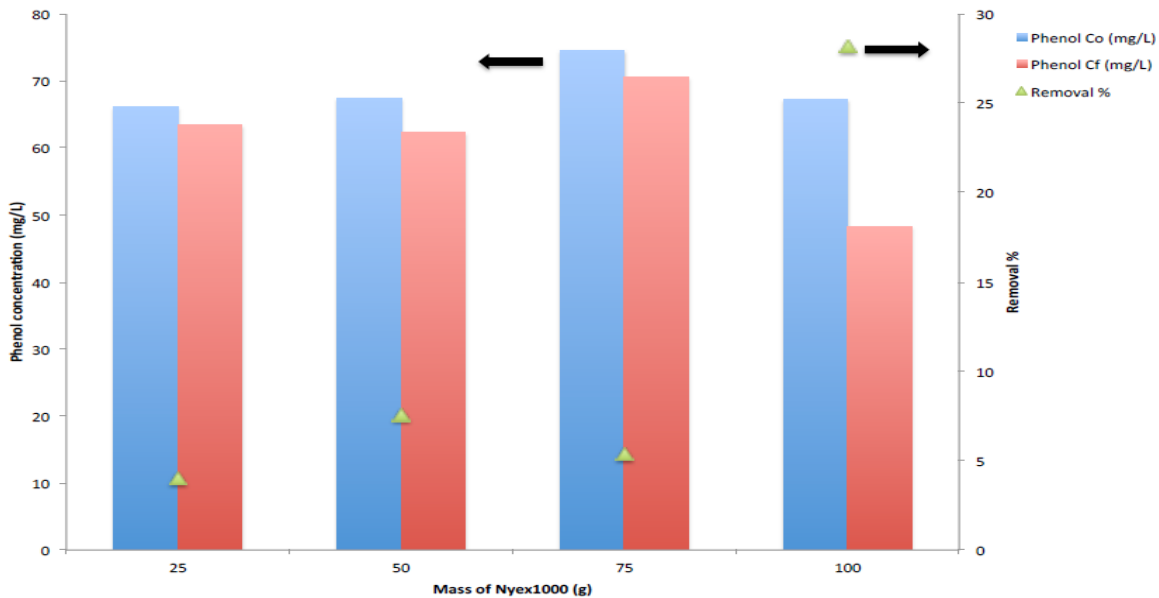


Fig. 3 Effect of adsorbent initial mass (Nyex=25, 50, 75, 100 g, time=60 min, v= 1L)

### III. RESULTS AND DISCUSSION

The effect of phenol initial concentration shows that total removal percentage (shown in Fig. 2) decreased from 44.21% to 20.86% when the initial phenol concentration increased from 37.08 mg/L to 161.08 mg/L with small quantity of adsorbent uptake that can be reflected by the organic substance solubility in aqueous phase and the adsorption mechanism of physical or chemical adsorption to the adsorbent surface. Indeed, the increment in the adsorbent initial mass enhanced phenol removal percentage from 4.03% to 28.19% when the adsorbent mass increased from 25 g to 100 g (Fig. 3) with an adsorbent phenol uptake of 0.18 mg/g when using 100 mg adsorbent Nyex1000.

In comparison, results of phenol removal with respect to adsorbent regeneration time using current of 1.368A for 10 min, regeneration efficiency reached 109.1% destroying accumulated adsorbed phenol of 0.133 mg/g at adsorbent surface and 112.5% using lower applied current of 1.2A for

time of 8 min targeting 0.072 mg/g adsorbed phenol. To conclude, theoretical charges to oxidize adsorbed phenol of 0.133 mg/g and 0.072 mg/g were 3.82 C/g and 2.07 C/g with respect to the measured charge of 10.08 C/g and 7.2 C/g, respectively. However, both applied current yield a current efficiency of 37.58% and 28.7% with respect to the theoretical required charge to oxidize 1 mole of phenol which is 206.7 coulomb. These finding indicates that applied charges for both experiments were not fully used to oxidize adsorbed phenol at the adsorbent surface (Fig. 4).

To investigate the fate of pollutants in the solid phase and clarify the effect of electrochemical regeneration in adsorbent Nyex1000, particles of adsorbent Nyex1000 were subjected to a coordinated set of surface analyses. Following preparation, particles were examined using SEM, then were subjected to a program of sputtering and ToF-SIMS before being examined once again using SEM and finally AFM.

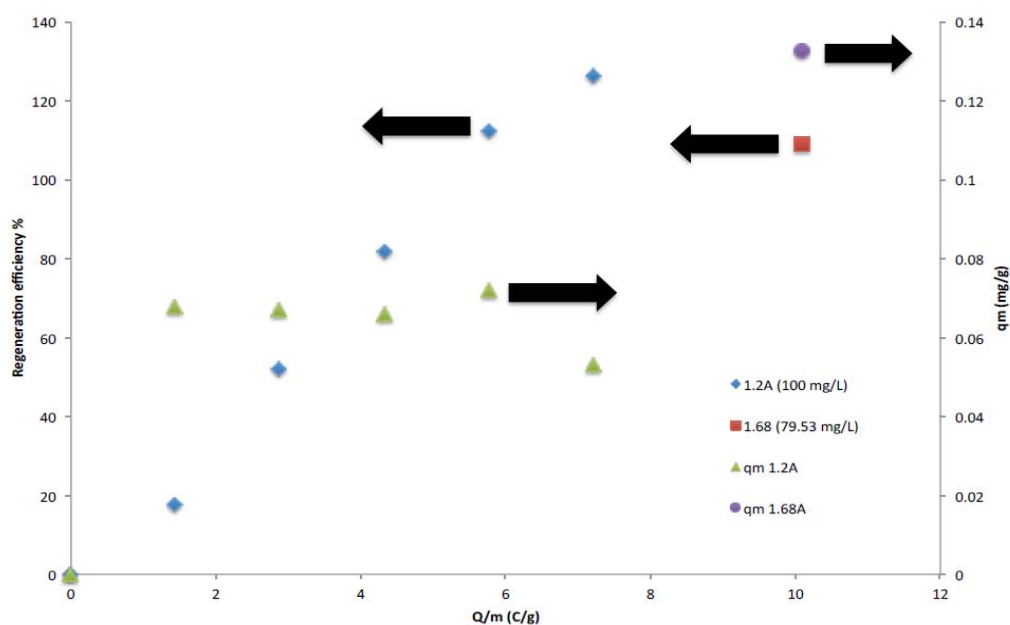


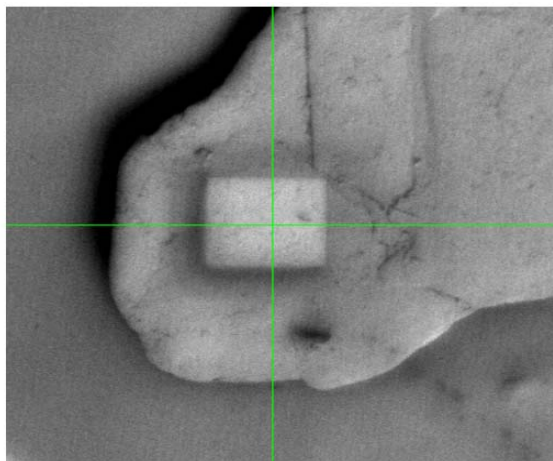
Fig. 4 Effect of regeneration time (Nyex1000 mass= 100g, adsorption time= 60 min, v= 1 L, electrolyte conc.= 0.3% NaCl)

Following phenol adsorption with initial concentration ( $C_0$ ) of 103 mg/L, 97.7 mg/L phenol remained in solution indicating a loading of 0.053 mg/g. Following the second adsorption  $C_0$  102.4 mg/L (after electrochemical regeneration), 95.7 mg/L of phenol remained in the solution indicating a loading of 0.067 mg/g. The regeneration efficiency was 126%. Based on the initial loading, the regeneration current efficiency was 21%. The composition of the adsorbent surface was studied using ToF-SIMS analysis with a gold ion incident beam. Fig. 5 shows two images that represent the impact of ToF-SIMS analysis as adsorbent particle rastered by the instrument element gold beam. Image (a) in Fig. 5 was captured by ToF-SIMS instrument immediately after analysis and image (b) is taken by SEM in

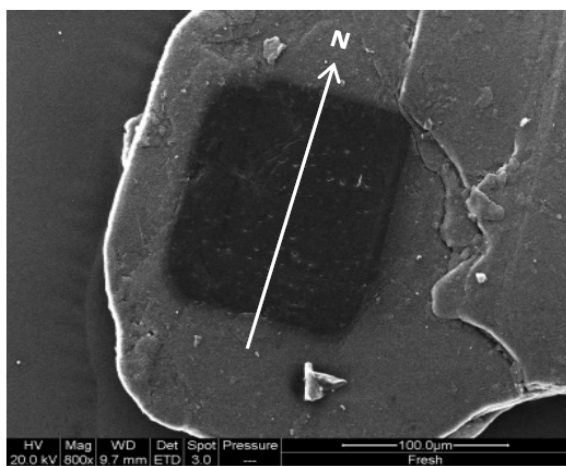
order to measure and visualize clearly the sputtered area on an adsorbent Nyex1000 particle. The sputtered area during the process is indicated as a dark rectangle rotated by approximately 15° with respect to the image margin and measuring approximately 150  $\mu\text{m}$  across. The white arrow indicates an arbitrary “North South” orientation for reference purposes.

Since adsorbent Nyex1000 is predominantly carbon (98%), the abundances of secondary ions detected are all expressed relative to the abundance of  $\text{C}^+$ . Three particles drawn from a single batch of adsorbent Nyex1000 were examined. The first, termed “Fresh” was drawn from the new batch. The second, named “Loaded” was drawn from the batch following the phenol adsorption and the third, termed “Regenerated”, was

drawn from the batch following subsequent electrochemical regeneration. Results of analysis shown in Fig. 6 revealed many ions but only three ions were possible to indicate phenol adsorption including  $C_2H_3$ ,  $CO$ , and  $C_2$ . The presence of these three ions were justified in comparison with the three investigated adsorbent particles including fresh, loaded, and regenerated. Within this set, the relative abundances of  $CO$ ,  $C_2H_3$ , and  $C_2$  showed the most significant differences between the loaded adsorbent Nyex1000 particle and the other two including fresh and regenerated. This leads to the conclusion that together they were indicative of the presence of phenol.



(a)

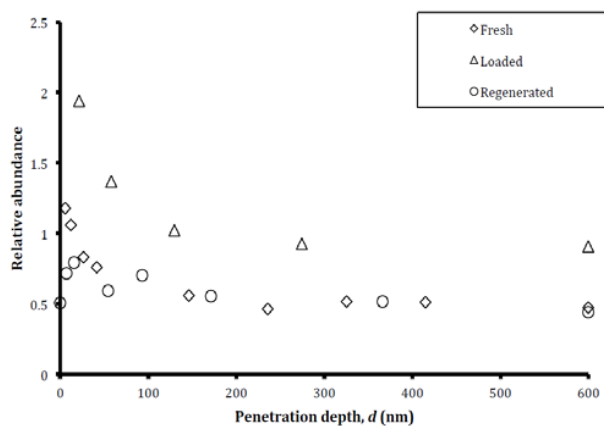


(b)

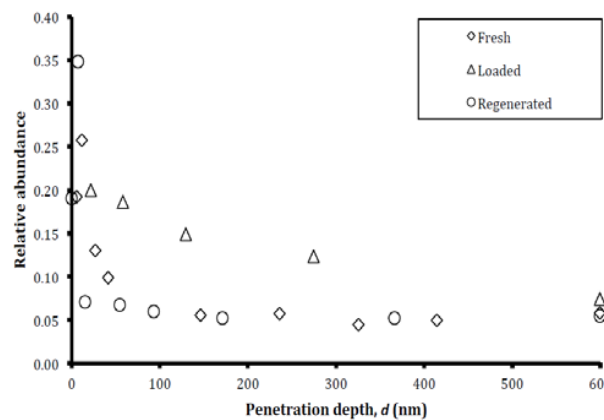
Fig. 5 Image of fresh Nyex1000 adsorbent taken by (a) ToF-SIMS and (b) SEM

The results show that the electrochemical regeneration step effectively removes phenol from the adsorbent and oxidizes the adsorbent surface, thus creating additional active hydroxyl sites for subsequent adsorption steps, while the enhanced equilibrium loading approves the implication that a proportion

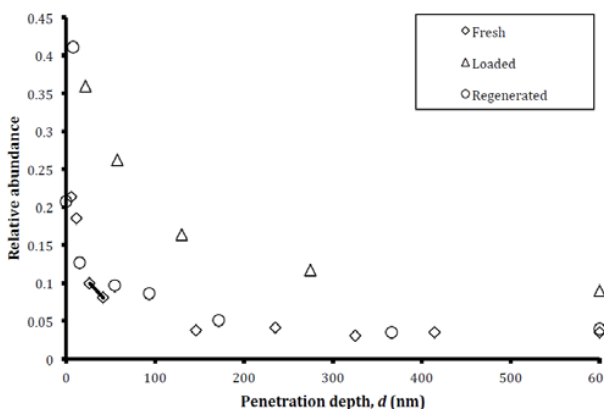
of the adsorbent has been lost to oxidation products and that this proportion is significant in relationship to the phenol removed from the wastewater.



(a)



(b)



(c)

Fig. 6 Relative abundance if three secondary ion fragments with respect to adsorbent depth (a)  $C_2H_3$ , (b)  $C_2$ , (c)  $CO$

## IV. CONCLUSION

Area averaged secondary ion relative abundances from the 'fresh' adsorbent show that the exposed surface is enriched in both hydrogen and oxygen indicating the presence of both hydride and hydroxyl groups on the perimeters of the graphene sheets. The enrichment also indicates the relative decrease in the area of individual graphene sheets as the exposed surface is approached. Following electrochemical regeneration, the surface hydrogen enrichment is significantly reduced, while the oxygen enrichment is similar to the 'fresh' adsorbent indicating that the surface has been oxidized.

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