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ORIGINAL PAPER

Electrochemical pre-treatment of effluents containing chlorinated compounds using an adsorbent

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Abstract Electrochemical pre-treatment of industrial wastewater to remove refractory and/or toxic organic components, making them more amenable to biological treatment, is likely to be more cost-effective than using a physical or chemical process for complete organic removal. This paper demonstrates the use of a carbon-based adsorbent material that preferentially removes chlorinated organic compounds. Electrochemical regeneration of the adsorbent is shown to be a quick, easy and cheap process, because the adsorbent is both highly electrically conducting and non-porous. High regeneration rates over a number of cycles were obtained by passing a charge of 25 C g^{-1} through a bed of adsorbent particles, at a current density of 20 mA cm^{-2} for 10 min. The energy required to remove a kg of COD from an industrial wastewater was calculated to be 27 kWh.

Keywords Nyex · Preferential adsorption · Phenol · Chlorinated phenols · Electrochemical regeneration · Pre-treatment · Industrial wastewater

1 Introduction

Whilst biological processes are usually the most cost effective methods for the removal of organic contaminants from effluents, the presence of toxic and/or non-biodegradable organics can render these processes ineffective, so chemical/physical methods are required. Increased public concern and the ability to detect trace levels of these compounds have resulted in increasing pressure on industry to remove these compounds to very low levels.

Adsorption onto activated carbon is one of the most attractive processes for this application as very low discharge consents can be achieved. However, activated carbon is non-specific in its removal and when heavily polluted waters are treated, it can result in the carbon being fully loaded very quickly. Once the activated carbon has been exhausted, it must be disposed of (by landfill or incineration) or regenerated. Regeneration is widely used, as it often represents the most commercially viable and environmentally acceptable alternative [1]. Thermal regeneration is the most widely used industrial process. However, this is a high energy/high cost process often requiring transportation to off-site specialist regenerators and results in 5–10% material loss [2]. Hence, there has been research into alternative regeneration techniques, including chemical/solvent [3–5], microwave [6], ultrasonic [7], biological [8, 9], wet oxidative [10] and electrochemical.

Electrochemical regeneration of activated carbon has been shown to be effective with regeneration efficiencies in the order of 80–95% being achieved [11–14]. However, periods of about 5 h are required, with relatively low current densities in the order of 1–2 mA cm^{-2}.

Whilst electrochemical process have been shown to be effective in removing refractory organic components, the high cost of electrical power means that full mineralization can be expensive. An alternative approach that has been suggested is to pre-treat the effluent to remove refractory components, rendering it more amenable to biological treatment [15].

Over the last few years, the authors have worked on an alternative approach to adsorption and electrochemical

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regeneration, based on a proprietary carbon-based adsorbent material (Nyex) that is non-porous and highly electronically conducting [16, 17]. Previous work has demonstrated that both the adsorption and regeneration processes are very quick. About 88% of the equilibrium capacity is utilised within 2 min and regeneration is achieved in 10 min passing a charge of 25 C g^{-1} at a current density of 20 mA cm^{-2}. Note that the charge passed was significantly greater than would be expected for double layer charging, indicating that Faradaic processes were occurring. It is likely that the anodic regeneration led to electrochemical oxidation of the adsorbed organic species. This work has shown that low discharge consents can be achieved (for example, atrazine removal to below 1 μg dm^{-3}) with multiple cycling at high regeneration efficiencies (100%) [16, 17].

Whilst previous work has shown that Nyex is a low capacity adsorbent, this paper reports results demonstrating its use to remove chlorinated compounds preferentially, in the pre-treatment of an industrial wastewater.

2 Materials and methods

Nyex 100 was supplied by Nykin Developments (Crewe, UK), which is developing Nyex as an adsorbent for water treatment, in the form of a wet powder with an average dry solids content of 50%. It has a carbon content of over 95% with a mean particle diameter of 127 μm and a range of particle sizes from 10 to 600 μm. The surface area of 2.75 m^2 g^{-1} is very low compared with activated carbon specific surface areas of up to 2,000 m^2 g^{-1}. Mercury porosimetry indicated that there were essentially no pores in the material, so explaining the low surface areas. All other chemical were supplied as analytical grade by Sigma-Aldrich UK.

2.1 Adsorption studies

Adsorption isotherms were constructed by mixing a range of known masses of Nyex with 100 cm^3 samples of deionised water (>13 MΩ cm) containing 100 mg dm^{-3} of phenol or chlorinated phenol in a 250 cm^3 flask and mixing for 30 min (which has been found to be sufficient to achieve equilibrium [17]). After adsorption, the samples were vacuum filtered and analysed by GC (Sect. 2.4).

Competitive adsorption was investigated by mixing a range of known masses of Nyex with 100 cm^3 of a mixed phenol/chlorinated phenol solution containing approximately 60 mg dm^{-3} of phenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. After mixing for 30 min, the solution was vacuum filtered and analysed by GC (Sect. 2.4).

2.2 Adsorption and electrochemical regeneration

Regeneration was achieved using an electrochemical cell divided into anode and cathode compartments by a microporous polypropylene Daramic 350 (supplied by Grace gmbh) membrane (Fig. 1). The cathode was perforated 316 stainless steel and the anode was a mixed metal oxide coated titanium (supplied by Electrode Products Technology Ltd, Coldicot, UK). The active area of each electrode was 22.5 cm^2, with 10 mm thick anode and cathode compartments. About 2% w/w NaCl solution was used as the catholyte. Constant current was supplied by a Thurlby Thandar Instruments power source (PL320QMD).

The procedure to determine the regeneration efficiency was:

(i) Initial adsorption—25 g of wet Nyex 100 was added to 100 cm^3 of 100 mg dm^{-3} phenol solution in a 250 cm^3 flask and mixed for 30 min. After adsorption, the flask's contents were vacuum filtered (Whatman GF/C) and the phenol and COD concentration of the filtrate determined.

(ii) Electrochemical regeneration—The loaded, filtered (but still wet, solids content approximately 50%) adsorbent was pressed into the anode compartment to make a bed 10 mm thick. In most cases, no additional electrolyte was added, but experiments to investigate chlorinated phenolic generation had solid sodium chloride added, to give a 2% sodium chloride concentration in the aqueous anolyte (Sect. 3.2). A 500 mA DC current (current density 20 mA cm^{-2}, optimised in earlier work [17]) was applied for regeneration times of 0–10 min. There was no flow in

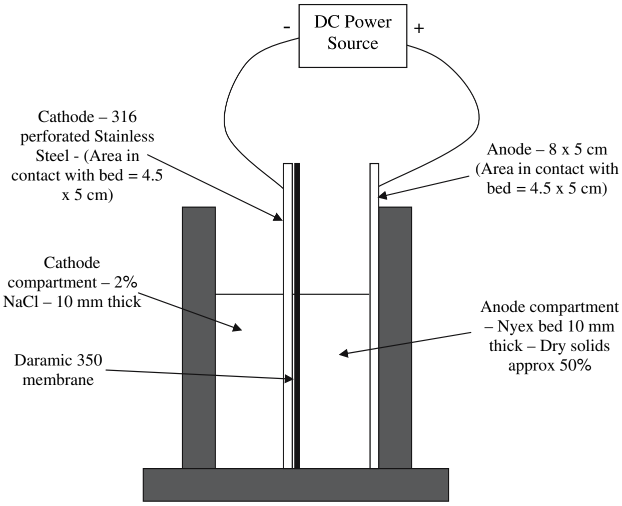

Fig. 1 Schematic diagram of the batch electrochemical regeneration cell

the cell and the only mixing was due to the gas bubbles produced at the electrodes.

(iii) Re-Adsorption—The full contents of the anode compartment were transferred to a 250 cm^3 flask and adsorption was undertaken using identical conditions to the initial step.

For the adsorption/electrochemical regeneration over a number of cycles, steps (ii) and (iii) were repeated.

The regeneration efficiency, RE, was calculated from:

$$\mathrm{RE} = \frac{q_\mathrm{r}}{q_\mathrm{i}} \times 100 \tag{1}$$

where q_i is the initial adsorptive capacity of fresh Nyex 100 (determined in step (i) above) and q_r is the adsorptive capacity of the regenerated material under identical adsorption conditions (step (iii) above).

The current efficiency (Φ^e) was calculated from:

$$\Phi^\mathrm{e} = \frac{\text{Theoretical charge required}}{\text{Actual charge passed}}$$

For the regeneration of an adsorbent material, the actual charge passed during regeneration was compared with the theoretical charge required for COD or phenol removed during the subsequent adsorption stage.

The current efficiency ($\Phi^\mathrm{e}_\mathrm{COD}$) for removal of COD was calculated using:

$$\Phi^\mathrm{e}_\mathrm{COD} = \frac{(\mathrm{COD_i} - \mathrm{COD_f})FV}{8It} \tag{2}$$

where $\mathrm{COD_i}$ and $\mathrm{COD_f}$ are the chemical oxygen demands before and after adsorption (g dm^{-3}) respectively, and I is the current (A), F is the Faraday Constant (96,487 C mol^{-1}) and V is the volume (dm^3) [18].

The current efficiency for phenol removal was calculated, based on the assumption that the phenol was completely mineralised to carbon dioxide by the reaction:

$$\mathrm{C_6H_5OH + 11H_2O \rightarrow 6CO_2 + 28H^+ + 28e^-}$$

Hence, the theoretical charge to mineralise the phenol can be calculated:

$$\mathrm{TC} = \frac{28(C_\mathrm{i} - C_\mathrm{f})VF}{94} \tag{3}$$

where C_i and C_f are the phenol concentrations before and after adsorption (g dm^{-3}). The current efficiency was calculated using

$$\Phi^\mathrm{e}_\mathrm{C_6H_5OH} = \frac{\mathrm{TC}}{It} \tag{4}$$

2.3 Industrial effluent treatment

An industrial effluent was supplied by United Utilities Industrial Ltd. (Daveyhulme, Manchester, UK) which contained a high organic content (filtered COD 11,070 mg dm^{-3}), with low levels of chlorinated compound, of which the most significant (98%) was dichloromethane (DCM) with a concentration of 137 mg dm^{-3}. About 100 cm^3 of this effluent was mixed with 25 g (wet, ca. 50% dry solids) Nyex 100 and was shaken for 30 min in a 250 dm^3 flask. This mixture was then vacuum filtered. A sample of the filtrate was taken and the rest retained for subsequent adsorptions. The wet solids were placed in the anode compartment and regenerated as in step (ii) above, but a regeneration current of 0.6 A was used. After regeneration, the solids were placed in the 250 cm^3 flask and were mixed with the remaining filtrate. These adsorption and regeneration cycles were repeated. Analysis of the samples was undertaken by United Utilities Industrial Ltd.

2.4 Analysis

The concentration of phenol and chlorinated phenols were determined using a Varian CP 3800 GC fitted with a FID detector. The column used a stationary phase of dimethyl polysiloxane. Some of the possible breakdown products from the electrochemical oxidation of phenol (benzoquinone, hydroquinone, catechol, oxalic, maleic and fumaric acids [18]) were determined using HPLC, with a mobile phase of methanol and water, using a Gemini column supplied by Phenomenex (Macclesfield, UK). Prior to their injection, the aqueous samples were filtered through a 0.45 μm Nylon filter. No other sample preparation was undertaken.

3 Results and discussion

3.1 Electrochemical regeneration

Electrochemical regeneration was achieved by passing a direct current through a bed of adsorbent particles with a dry solids content of approximately 50%. This was believed to result in the anodic oxidation of the organic contaminants. Herein we report the effect of varying the charge passed (0–25 C g^{-1}) over a number of cycles through a phenol-loaded Nyex, using a current density of 20 mA cm^{-2} (Fig. 2), at a typical cell voltage of ca. 5 V. Previous work had shown that 100% regeneration of Nyex loaded with crystal violet dye could be achieved by passing a current of 0.5 A (20 mA cm^{-2}) through the cell for 10 min [17], corresponding to a specific charge of around

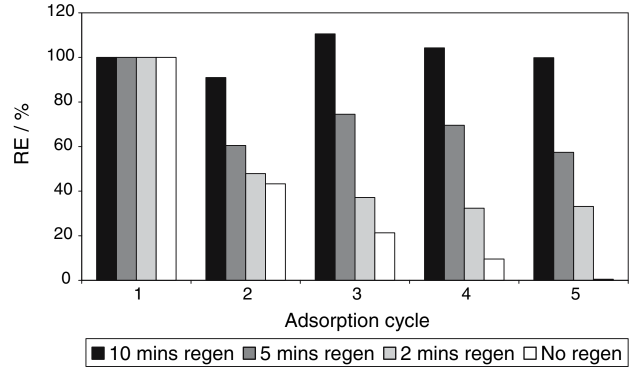

Fig. 2 Effect of number of adsorption/regeneration cycles on the regeneration efficiency of phenol loaded Nyex 100 for a range of regeneration charges. Cycle 1 was for a fresh Nyex 100 adsorbent. When no charge was passed (0 C g^{-1}) additional adsorption was observed over each cycle giving an apparent regeneration efficiency

25 C g^{-1} (dry solids). A similar result was obtained in this work with increasing regeneration times resulting in increased regeneration efficiencies. A regeneration efficiency of around 100% was achieved after 10 min.

When no charge was passed, there was still an apparent regeneration efficiency. This additional capacity can be explained by considering the shape of the adsorption isotherm, shown schematically in Fig. 3. After 1 adsorption cycle, a liquid phase equilibrium concentration, C_{e1}, results, giving a corresponding solid phase equilibrium concentration, q_{e1}. After a second adsorption cycle (with no regeneration), the liquid phase equilibrium concentration will be C_{e2}. This gives a corresponding solid phase concentration of q_{e2}. Since there was already a quantity of adsorbate on the adsorbent, q_{e1}, the additional adsorbate taken up would be $\Delta q = q_{e2}–q_e$; hence, the additional adsorptive capacity of Nyex without regeneration.

In addition, the COD and phenol concentrations were analysed in the filtrate after adsorption. These results are shown in Fig. 4, in which the ratio of COD and phenol concentrations, before and after adsorption, show very similar trends. This suggested that the phenol was eliminated from the effluent, without the formation of significant quantities of breakdown products. As shown in Table 1, this was confirmed by calculating the current efficiencies required to remove the phenol and COD, which show very similar values; those greater than 100% were due to adsorption and dilution effects (the Nyex is supplied wet).

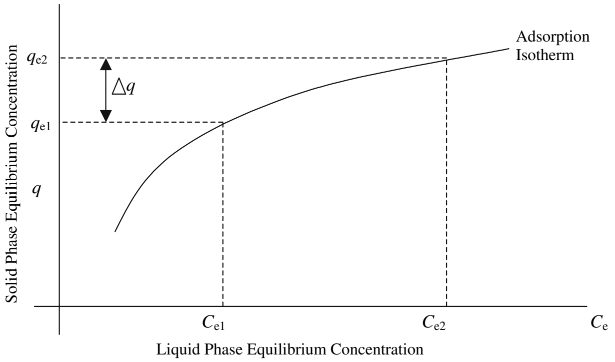

Fig. 3 Schematic representation of the adsorptive capacity of loaded adsorbent

Analysis of the resulting filtrate for some of the main electrochemical breakdown products of phenol, found only small quantities, suggesting that few breakdown products were produced or desorbed, even when the regeneration charge was insufficient for 100% regeneration (Fig. 5). Whilst the fate of the adsorbed phenol has yet to be fully determined, the data presented suggested that the organic compounds were oxidised during regeneration without being released. The breakdown products may have remained adsorbed onto the Nyex or may been released as carbon dioxide or volatile organic compounds. Analysis of the adsorbed species will be required to determine if the breakdown products were adsorbed on the Nyex. However, since the adsorptive capacity of regenerated (10 min regeneration) Nyex was very similar to fresh Nyex, the results suggested that the breakdown products were not adsorbed on the surface; hence, we believed that the phenol had been mineralised. This was particularly likely, as 100% regeneration could be achieved over a number of cycles.

Comninellis has suggested that electrochemical oxidation of organics occurs at electrodes through the generation of hydroxyl radicals that are either physisorbed (non-active electrodes) or chemisorbed (active electrodes) [19], with full mineralization of phenol being achieved at non-active (for example boron-doped diamond) electrodes. The lack of breakdown products suggested that the Nyex surface acted as a non-active electrode. An alternative possibility was that direct electron transfer may have occurred as the organic was adsorbed strongly on the Nyex surface. This would appear to be a different mechanism to the electrochemical regeneration of activated carbon, for which it has been suggested that desorption of the phenol occurs prior to oxidation [11]. However, Canizares et al. [20] have also suggested that electrochemical regeneration of phenol-loaded activated carbon results by direct oxidation of phenol to carbon dioxide. This is an area where further research is required.

The electrical energy requirement to remove a kg of COD was calculated as 6.6–22 kWh kg^{-1} COD, with the lower values resulting from some dilution and adsorption effects, and the higher values being needed to achieve 100% regeneration efficiencies. This compares with a value of 63.02 kWh kg^{-1} COD achieved by Canizares et al. [20] for the 80% regeneration of a granular activated carbon loaded with phenol.

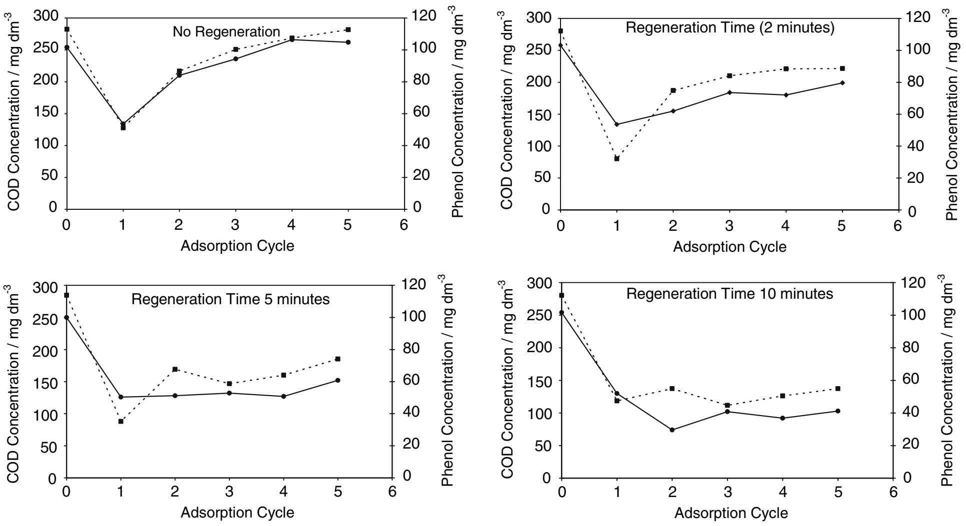

Fig. 4 Concentration of phenol and COD in the filtrate after adsorption for a series of cycles for a range of different regeneration times. Cycle 0 is initial concentration of COD and phenol: (●) COD; (■) Phenol

Table 1 Calculated current efficiencies for COD and phenol removal. The quoted values are the average values over the 5 adsorption cycles

Regeneration time (mins)	Current efficiency phenol, Φ^{e}_{phenol} (%)	Current efficiency COD, Φ^{e}_{COD} (%)
2	135	158
5	91	93
10	58	65

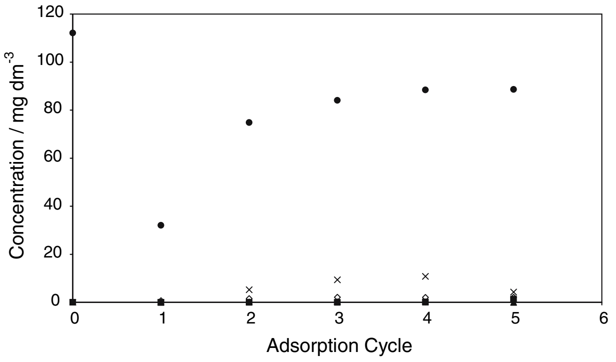

Fig. 5 Concentration of electrochemical breakdown products of phenol in the filtrate after a series of phenol adsorption/regeneration cycles with a regeneration time of 2 min (charge passed 5 C g^{-1}). No fumaric acid or catechol were detected: (◇) Oxalic; (■) Maleic; (▲) Hydroquinone; (×) Benzoquinone; (●) Phenol

3.2 Chlorinated phenol

Previous work has shown that the use of sodium chloride, as a supporting electrolyte in the anode compartment, resulted in a small increase in regeneration efficiency. However, it was also found that the conductivity of the Nyex bed was sufficiently high to allow regeneration to occur at a low cell voltage which remained relatively constant during regeneration, without the use of a supporting electrolyte [21]. From an industrial perspective, it was believed that eliminating chemical addition would be more advantageous than achieving slightly higher regeneration efficiencies. Hence, most trials were undertake without the use of supporting electrolyte in the anode compartment.

However, many industrial effluents already contain sodium chloride [22] and this presence of sodium chloride during electrochemical treatment of phenol-containing wastewater has been shown to result in the production of chlorinated compounds [23, 24]. This is potentially significant, as these products may be more toxic than the original phenol. In order to investigate the potential for the generation of chlorinated phenol compounds during Nyex regeneration, a series of experiments was undertaken with sodium chloride present in the anode compartment at an aqueous concentration of 2%.

A trial was undertaken to regenerate phenol loaded Nyex using 2% wt/wt NaCl as supporting electrolyte within the anode compartment. Analysis of the filtrates for 2-chloro, 2,4 dichloro and 2,4,6 tri-chloro phenols found only trace levels of 2-chlorophenol in two of the samples after regeneration. Surprisingly, essentially no chlorinated phenols were detected, even when the charge passed was insufficient for 100% regeneration, so adsorption isotherms for these compounds were determined to investigate why (Fig. 6). Previous work had demonstrated that these isotherms could be modelled using the Freundlich equation [17]. It was found that increasing the degree of chlorination strongly influenced the adsorptive capacity. A similar effect of increased adsorption of chlorinated phenols onto granular activated carbon (GAC) has also been reported, for example by Streat et al. [25] and Juang et al. [26].

Since Nyex is a carbon-based material, it seemed reasonable, as a first assumption, that phenol adsorption occurred via a similar mechanism to that proposed for

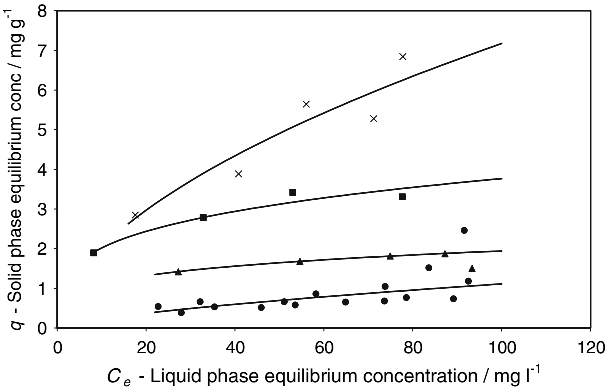

Fig. 6 Adsorption isotherms for phenol and chlorinated phenols onto fresh Nyex 100 in a 250 cm^3 flask using a contact time of 30 min to achieve equilibrium. Solid lines show Freundlich adsorption isotherms fitted to the data: (●) Phenol; (▲) Chlorophenol; (■) Dichlorophenol; (×) Trichlorophenol

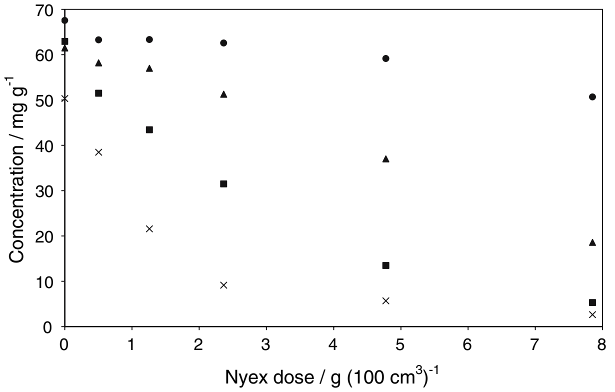

Fig. 7 Filtrate phenol and chlorinated phenol concentrations after adsorption on Nyex 100, with a range of doses. Initial concentration approximately 60 mg dm^{-3} of 2,4,6-trichlorophenol, 2,4-di-chlorophenol, 4, chlorophenol and phenol: (●) Phenol; (▲) Chlorophenol; (■) Dichlorophenol; (×) Trichlorophenol

activated carbon. Adsorption of aromatic molecules onto the surface of activated carbons has been reported to occur through a donor-acceptor mechanism. Carboxyl oxygen groups on the carbon surface act as electron donors, whilst the aromatic rings in the chlorinated phenol behave as electron acceptors [27]. Chlorination of phenol decreases the electron density within the π-system of the aromatic ring, due to the greater electronegativity of chlorine. This is likely to increase the adsorption density of chlorophenols compared with phenol, increasing chlorine substitution of the aromatic ring lowering the electron density of the π-system and enhancing adsorption.

Figure 7 shows that when various quantities of Nyex were contacted with a solution containing approximately equal concentrations (60 mg dm^{-3}) of phenol, mono-, di- and tri-chlorinated phenols, the extent of adsorption decreased in the order tri-chloro > di-chloro > monochloro > non-chlorinated phenol; i.e., adsorption densities increased with degree of chlorination of phenol.

Analysis of partially regenerated adsorbent (charge passed 12.5 C g^{-1}) washed in deionised water detected no release of chlorinated compounds. Hence, any chlorinated compounds produced appear to remain bound to the adsorbent surface. This is consistent with the earlier results (Sect. 3.1) which suggested that breakdown products were not released during regeneration and subsequent adsorption.

3.3 Industrial effluent treatment

This preferential adsorption of chlorinated compounds could be exploited for the pre-treatment of biodegradable wastes containing toxic chlorinated compounds, potentially providing a method for selective elimination of the chlorinated compounds, leaving an effluent that is amenable to lower cost biological treatment.

An example of this type of effluent (containing a high organic content and including 137 mg dm^{-3} dichloromethane (DCM)) was provided by United Utilities Industrial Ltd. As shown in Fig. 8, treatment with Nyex led to a linear removal of COD for each adsorption/regeneration cycle after the first cycle. The first cycle introduced some dilution as the Nyex was supplied wet. This linear removal indicates that the conditions used achieved 100% regeneration. However, the results showed that, after one cycle of adsorption, 99% of the DCM was removed. It is likely that after the effluent has been treated by one cycle of adsorption and regeneration, it would be suitable for biological treatment, although further work is required to confirm this.

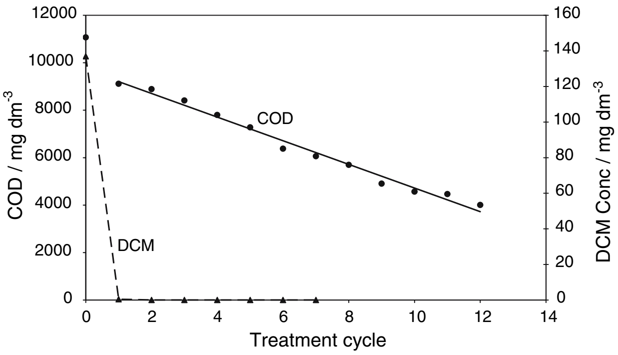

Fig. 8 Comparison of the removal of COD and di-chloromethane (DCM) from an industrial effluent containing a complex mixture of organic contaminants over a number of adsorption/regeneration cycles: (●) COD; (▲) Dichloromethane

The cell potential was found to remain approximately constant at 6 V when a current of 0.6 A (current density 24 mA cm^{-2}) was passed through the cell, corresponding to 27 kWh per kg of COD removed. This compares with a specific electrical energy consumption of 21 kWh kg^{-1} COD for the electrochemical oxidation of COD in a textile dye wastewater at a Ti/Pt anodes [28] and 30–50 kWh kg^{-1} COD at highly doped SnO_2 anodes [29]. If a biodegradable effluent can be produced by the adsorption-electrochemical regeneration process, this approach is likely to be very cost effective. Based on a unit electrical cost of £0.1 kWh^{-1}, the cost of electrical energy to pre-treat this effluent would have been only £0.9 m^{-3}.

4 Conclusions

Electrochemical regeneration of a phenol–loaded, non-porous adsorbent material, Nyex 100, was achieved by passing a charge of about 25 C g^{-1} through a bed of Nyex particles without the use of a supporting electrolyte. In addition, the presence of sodium chloride during regeneration did not result in the release of chlorinated phenolic compounds, probably due to an increased adsorptive capacity for these compounds on the Nyex. Not only did the Nyex have increased adsorptive capacity for chlorinated compounds, but also that these compounds were adsorbed preferentially.

In addition, it was found that Nyex adsorption and electrochemical regeneration could be used to pre-treat a wastewater contaminated by low levels of chlorinated waste, rendering it more amenable to biological treatment. The pre-treatment costs for such a process were found to be £0.9 per m^3. This approach would offer significant savings when compared to complete removal of the organic content by alternative physical or chemical processes.

The results suggested that the energy requirement to pre-treat such an industrial waste would be 27 kWh kg^{-1} COD removed, which is towards the low end of energy consumption figures for such electrochemical treatments reported in the literature. This was due to the highly conducting nature of the Nyex.

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