Electronic Supplementary Material (ESI) for Analyst.

Supporting Information Section

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1. Optimising the Paste Composition to Achieve Highest Target Uptake

1.1. Equilibrating the Four Carbon Pastes With 4-Phenoxyphenol

The electrochemical behaviour of 4-phenoxyphenol was first investigated, using the four carbon paste electrodes, with the aim of quantifying the equilibration of the pastes with the analyte as well as comparing the electrochemical responses.

Four carbon paste electrodes, fabricated by mixing graphite powder with dioctyl phthalate, graphite powder with mineral oil, nanocarbon with mineral oil and nanocarbon with dioctyl phthalate, were used to record and compare the cyclic voltammetric responses of phenol, 4-phenoxyphenol and 4-methoxyphenol. Pre-concentration experiments were carried out to quantify the uptake of 4-phenoxyphenol and determine the necessary pre-concentration time of each electrode with phenol and 4-phenoxyphenol.

Each carbon paste electrode was immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 2.5 – 20 μM 4-phenoxyphenol and 0.1 M KCl as the supporting electrolyte. This was done under open circuit conditions, for progressively increasing pre-concentration times. The paste electrode was then transferred to a deoxygenated aqueous borate buffer solution of pH 10.01, which only contained 0.1 M KCl, and in which oxidative 100 mV s^{-1} cyclic voltammetric scans were run, between 0.0 V and + 0.60 V (vs. SCE). Peaks due to the oxidation of 4-phenoxyphenol were seen a peak potentials of +0.43 V, +0.35 V, +0.38 V and +0.51 V (vs. SCE) on the graphite/dioctyl phthalate, graphite/mineral oil, nanocarbon/mineral oil and nanocarbon/dioctyl phthalate pastes respectively (Fig. SI-1).

The results obtained with the 20 μM 4-phenoxyphenol solution can be seen in Fig. SI-2a where, for all four pastes used, the peak current increased with increasing pre-concentration time and a plateau was reached at ca. 60 s (Fig. SI-2b). Fig. SI-2b also demonstrates the similar trends that were seen to be followed with the 2.5, 7.0 and 11 μM 4-phenoxyphenol solutions, again with all four pastes. The expected effect of higher currents being seen with increasing target concentration is also shown.

Considering Fig. SI-1, the observation that higher currents were seen with the graphite/dioctyl phthalate paste indicates a greater ability to uptake the target phenol. Examining Figs. SI-2a and SI-2b, the increase in peak height with increasing pre-concentration time, observed for each set of measurements at a given 4-phenoxyphenol concentration, for all four pastes, is consistent with increasing amounts of 4-phenoxyphenol being accumulated in each paste with increasing pre-concentration times. This is observed until the pastes are equilibrated with the analyte of interest, at which point the plateau is reached. Upon comparing the results obtained at different target concentrations for each paste, the increase in the produced currents with 4-phenoxyphenol concentration is again reasonable given that more and more 4-phenoxyphenol is present in solution and able to transfer into the paste.

Importantly, given the similar equilibration times of ca. 60 s that were observed for all pastes combined with the greater 4-phenoxyphenol uptake of the graphite/dioctyl phthalate paste, the choice of the graphite/dioctyl phthalate combination as the optimum one for further experiments with 4-phenoxyphenol was clear.

1.2 Equilibrating the Four Carbon Pastes With Phenol

The four pastes were next used to explore the uptake of phenol. Each carbon paste electrode was first immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 7.0 – 40 µM phenol and 0.1 M KCl as the supporting electrolyte. This was again done under open circuit conditions, for increasing pre-concentration times. Oxidative 100 mV s^{-1} cyclic voltammetric scans were then run, between -0.10 V and +0.70 V (vs. SCE), in a deoxygenated aqueous borate buffer solution of pH 10.01, which only contained 0.1 M KCl. Peaks corresponding to the oxidation of phenol were seen at peak potentials of +0.55 V, +0.54 V, 0.56 V and +0.62 V (vs. SCE), on the graphite/dioctyl phthalate, graphite/mineral oil, nanocarbon/mineral oil and nanocarbon/dioctyl phthalate pastes respectively (Fig. SI-3).

The results obtained with the 40 µM phenol solutions, on the graphite dioctyl phthalate paste, are shown in Fig. SI-4a. As in the case of 4-phenoxyphenol, the peak currents were again seen to increase with increasing pre-concentration time, though this time the plateau was reached after ca. 90 s. Higher currents were also again seen with the graphite/dioctyl phthalate paste (Fig. SI-3) and the four pastes were again equilibrated with the analyte at similar equilibration times, here of ca. 90 s (Fig. SI-4b). These results were not only consistent with more and more phenol being accumulated in the paste and then oxidised, up to the point at which the paste was equilibrated with phenol, but also confirmed the choice of the graphite/dioctyl phthalate paste as the optimum paste with which to carry out analogous phenol pre-concentration experiments with phenol solutions of concentrations 7.0 – 20 µM.

As expected, the peak current increased with increasing pre-concentration time, as illustrated in Fig. SI-5, where the plateau is seen to be reached at ca. 90 s, once the paste had been equilibrated with phenol. Again as anticipated, higher currents were observed when solutions of higher phenol concentrations were used as the source of phenol.

1.3 The Possible Variation of the Background Current With Immersion Time

Having optimised the paste composition and studied the uptake of phenol and 4-phenoxyphenol on the four paste electrodes, a short investigation was done into the effect of the immersion time of the paste electrodes in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 0.1 M KCl as the supporting electrolyte. Such experiments were needed given the shape of the voltammograms in Figs. SI-2a and SI-4a, where the diffusion tail of the measurements can be seen to change with increasing pre-concentration time with each analyte.

Each carbon paste electrode was thus left, under open circuit conditions, in a deoxygenated aqueous borate buffer solution of pH 10.01, which contained 0.1 M KCl as the supporting electrolyte, for increasing times, after which oxidative scans were run between -0.20 V and +0.60 V (vs. SCE). Typical scans are shown in Fig. SI-6, where the background current is seen to remain effectively constant throughout the experiment, leading to the conclusion that it was the organic analyte that was responsible for any changes previously observed.

Supporting Information Figures:

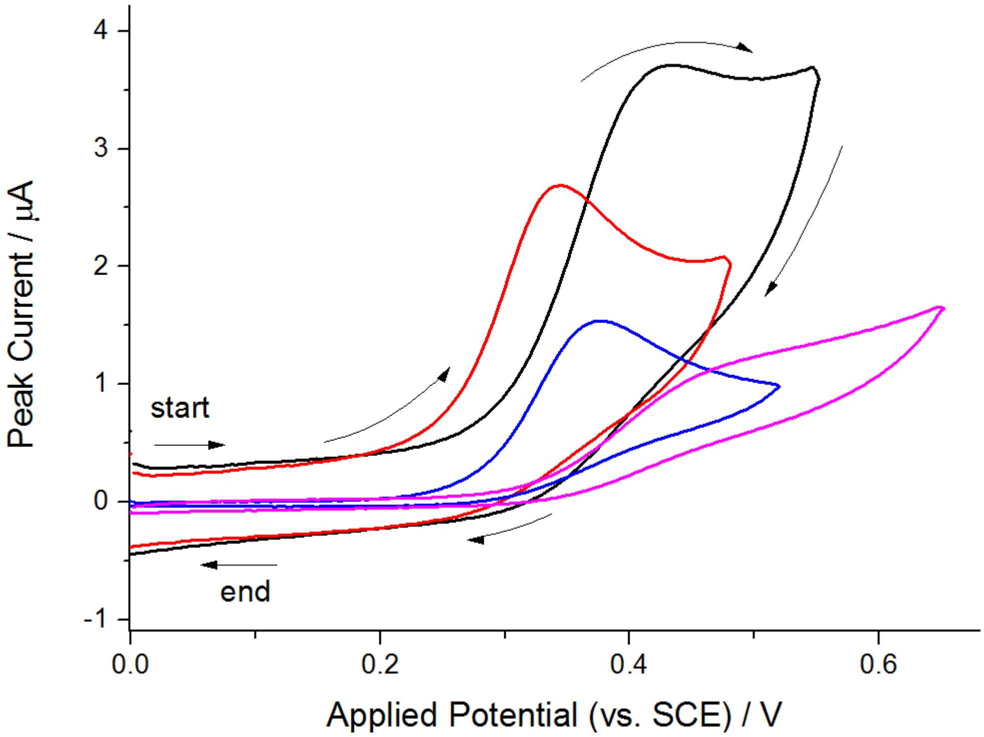

Fig. SI-1: Typical oxidative 100 mV s^{-1} voltammetric responses for the oxidation of 4-phenoxyphenol on the four carbon paste electrodes used; the oxidation of 4-phenoxyphenol to benzoquinone was seen to take place at +0.43 V, +0.35 V, +0.38 V and +0.51 V (vs. SCE) on the graphite/dioctyl phthalate (black), graphite/mineral oil (red), nanocarbon/mineral oil (blue) and nanocarbon/dioctyl phthalate paste (magenta), respectively. The scans were obtained in a deoxygenated BBS solutions (0.1 M KCl, pH=10.01, 298 K), after immersing each electrode in an identical solution that also contained 20 µM 4-phenoxyphenol for 60 s. Higher currents were observed with the graphite/dioctyl paste.

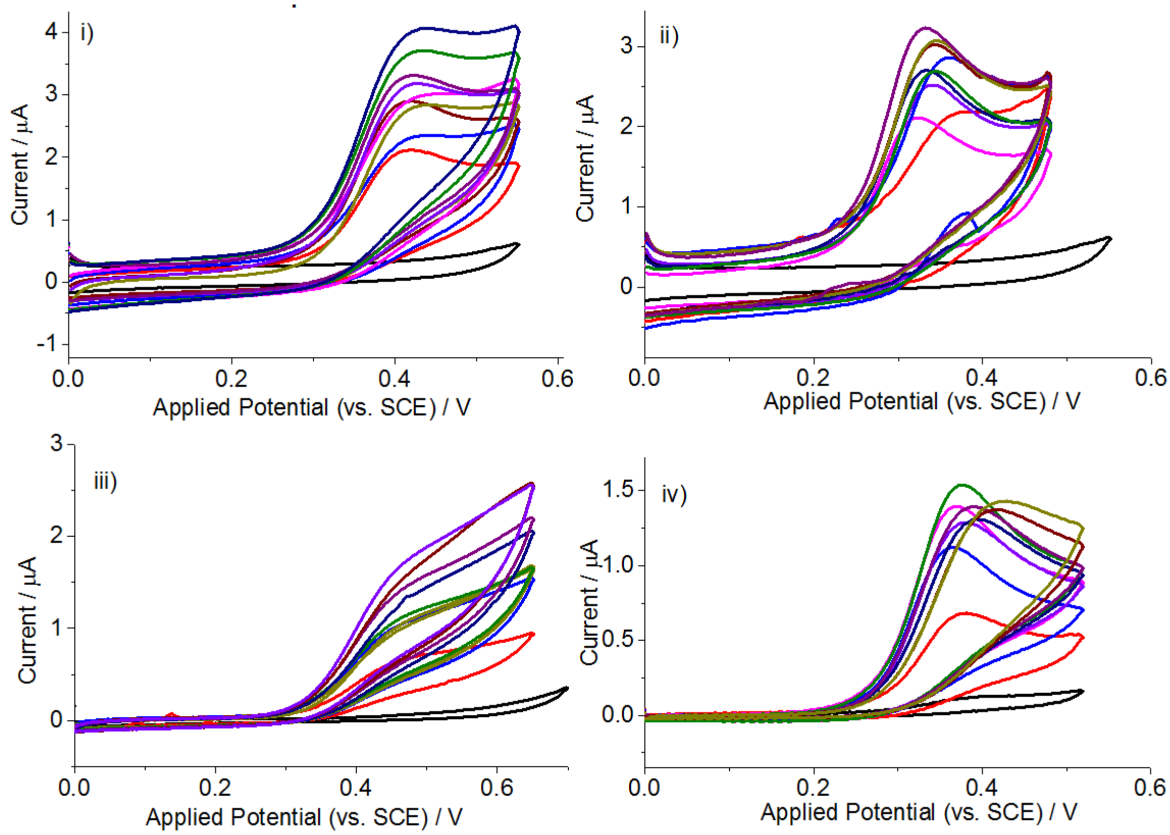

Fig. SI-2a: Oxidative 100 mV s^{-1} voltammetric responses for the oxidation of 4-phenoxyphenol to benzoquinone on the four carbon paste electrodes used (i: graphite/dioctyl phthalate, ii: graphite/ mineral oil, iii: nanocarbon/mineral oil, iv: nanocarbon/dioctyl phthalate). The scans were obtained in a deoxygenated BBS solution (0.1 M KCl, pH=10.01, 298 K), after immersing each electrode in an identical solution that also contained 20 µM 4-phenoxyphenol for increasing pre-concentration times between 0 s and 210 s. Higher currents can are seen with the graphite/dioctyl phthalate paste.

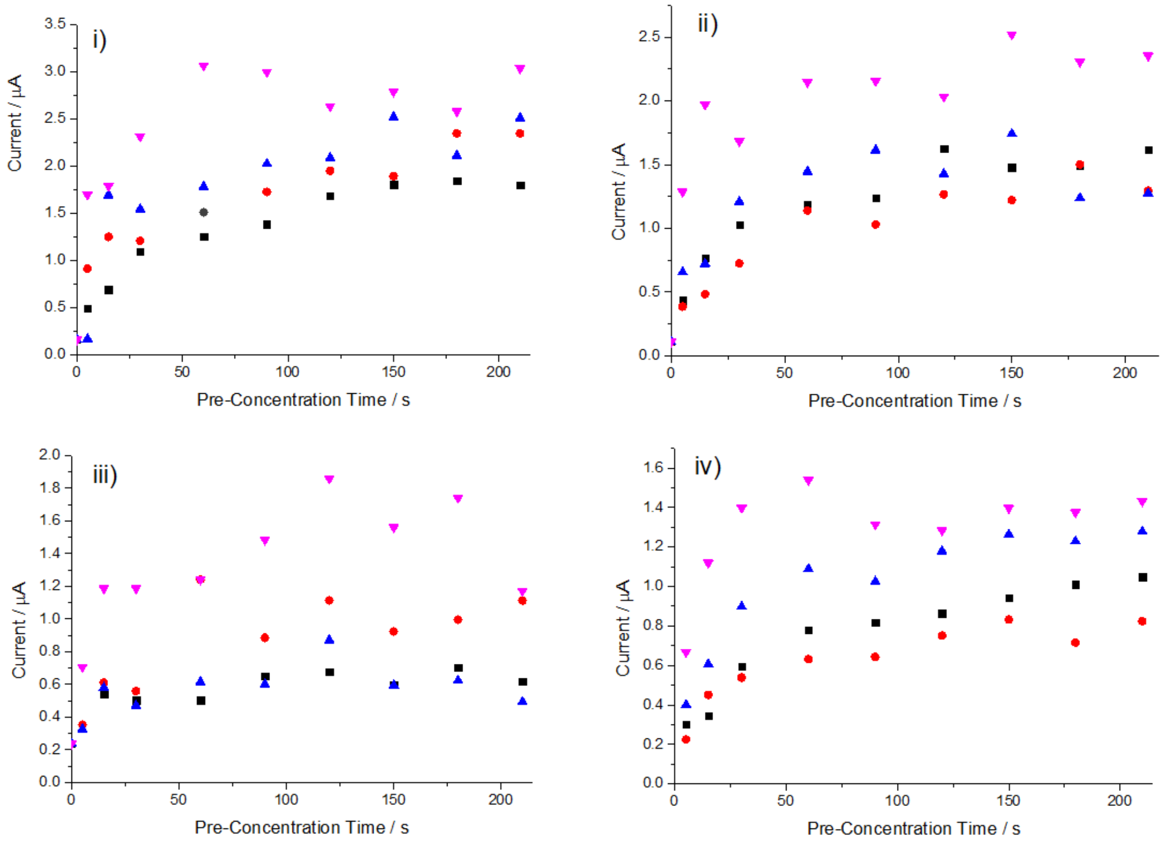

Fig. SI-2b: The variation of peak current with pre-concentration time of the responses obtained at different 4-phenoxyphenol concentrations (i: graphite/dioctyl phthalate, ii: graphite/ mineral oil, iii: nanocarbon/mineral oil, iv: nanocarbon/dioctyl phthalate, where black: 2.5 µM, red: 7.0 µM, blue: 11 µM and magenta: 20 µM). As expected, for all four pastes, the peak current increases with increasing pre-concentration time, reaching a plateau at around 60s; the paste in question is then assumed saturated with 4-phenoxyphenol. Also as expected, larger currents are observed with the larger 4-phenoxyphenol concentrations. Higher currents can are seen with the graphite/dioctyl phthalate paste.

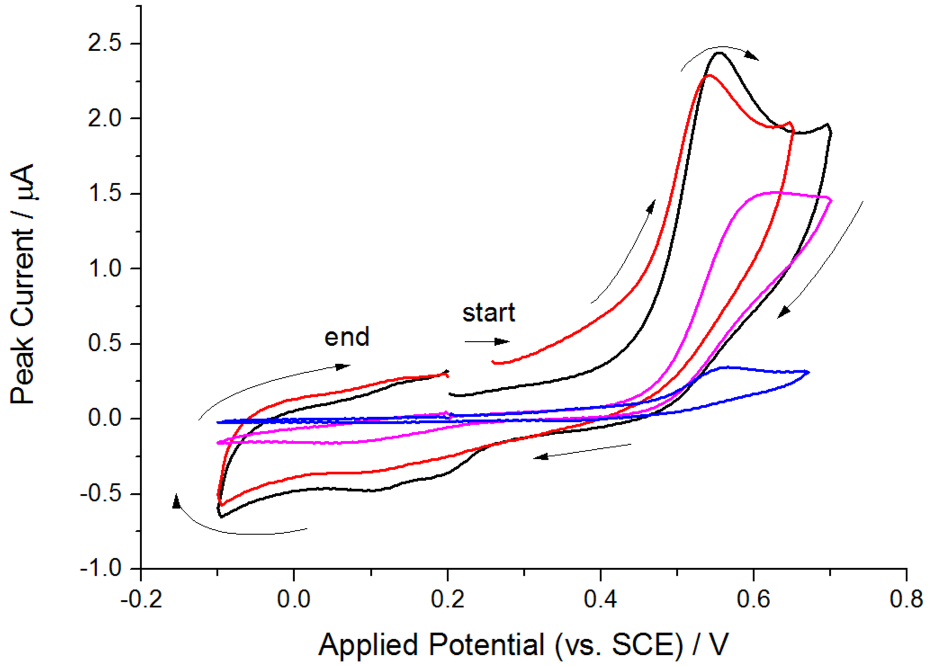

Fig. SI-3: Typical oxidative 100 mV s^{-1} voltammetric responses for the oxidation of phenol on the four carbon paste electrodes used (black: graphite/dioctyl phthalate, red: graphite/ mineral oil, blue: nanocarbon/mineral oil, magenta: nanocarbon/dioctyl phthalate). The scans were obtained in a deoxygenated BBS solution (0.1 M KCl, pH=10.01, 298 K), after immersing each electrode in an identical solution that also contained 40 µM phenol for 90 s. The oxidation of phenol was seen to take place between +0.54 and +0.62 V (vs. SCE). Higher currents were observed with the graphite/dioctyl paste.

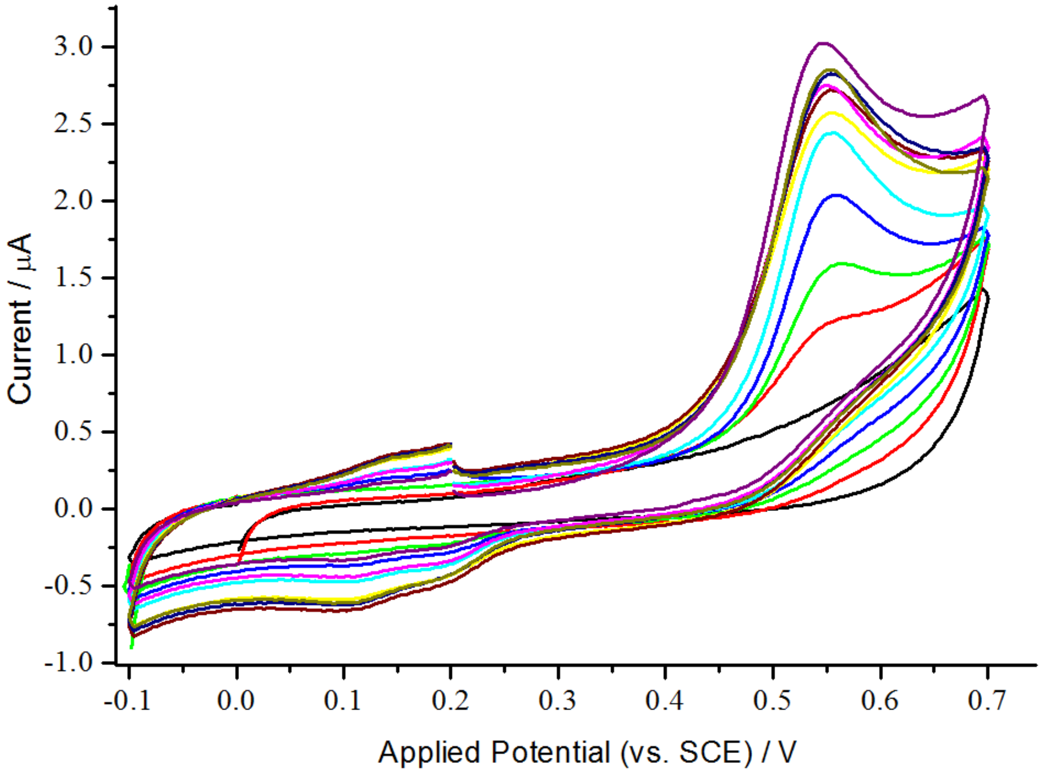

Fig. SI-4a: Oxidative 100 mV s^{-1} voltammetric responses for the oxidation of phenol on the graphite/dioctyl phthalate paste. The scans were obtained in a deoxygenated BBS solution (0.1 M KCl, pH=10.01, 298 K), after immersing each electrode in an identical solution that also contained 40 μM phenol for increasing pre-concentration times between 0 s and 240 s.

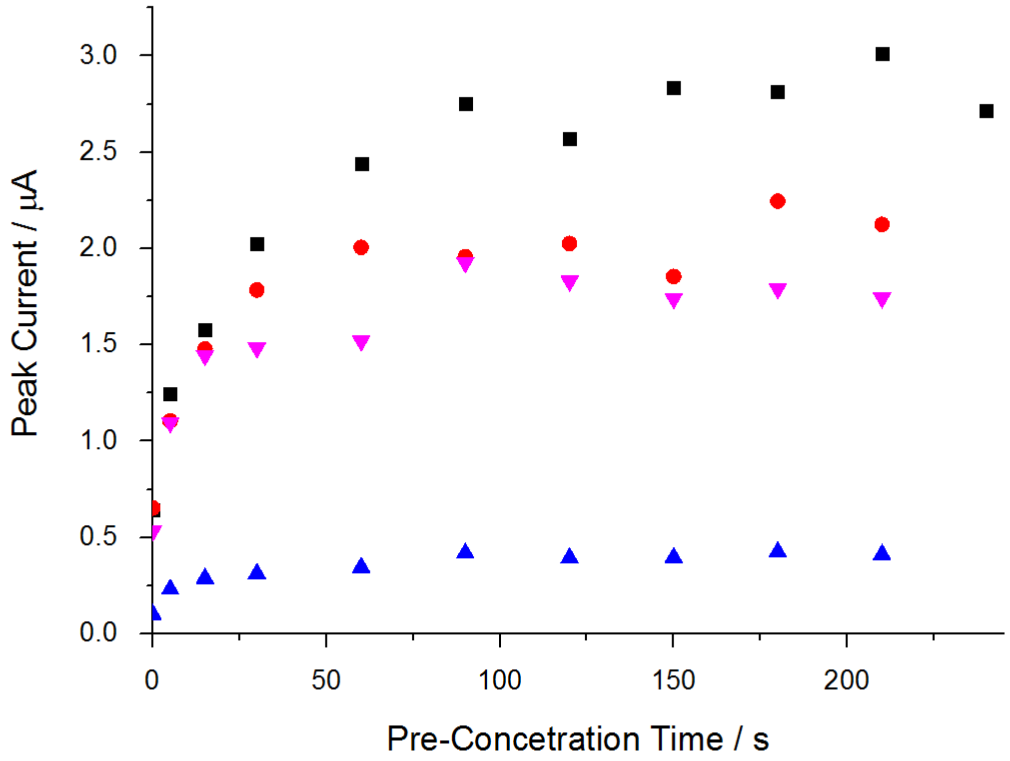

Fig. SI-4b: The variation of peak current of the responses with pre-concentration time (black: graphite/dioctyl phthalate, red: graphite/ mineral oil, blue: nanocarbon/mineral oil, magenta: nanocarbon/dioctyl phthalate). For all four pastes, the peak current increases with increasing pre-concentration time, reaching a plateau at ca. 90s; all pastes are then assumed saturated with phenol.

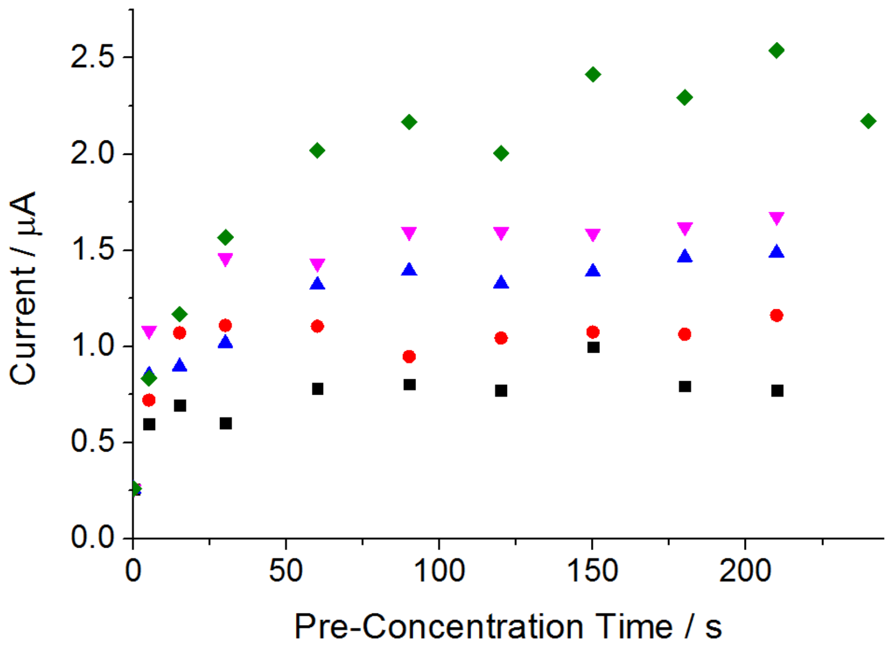

Fig. SI-5: The variation of peak current with pre-concentration time of the responses obtained at different phenol concentrations, for the graphite/ dioctyl phthalate paste (where black: 7.0 µM, red: 9.5 µM, blue: 13 µM, magenta: 20 µM and olive: 40 µM). As expected, the peak current increases with increasing pre-concentration time, reaching a plateau at around 90s; the paste in question is then assumed saturated with phenol. Also as expected, larger currents are observed with the larger phenol concentrations.

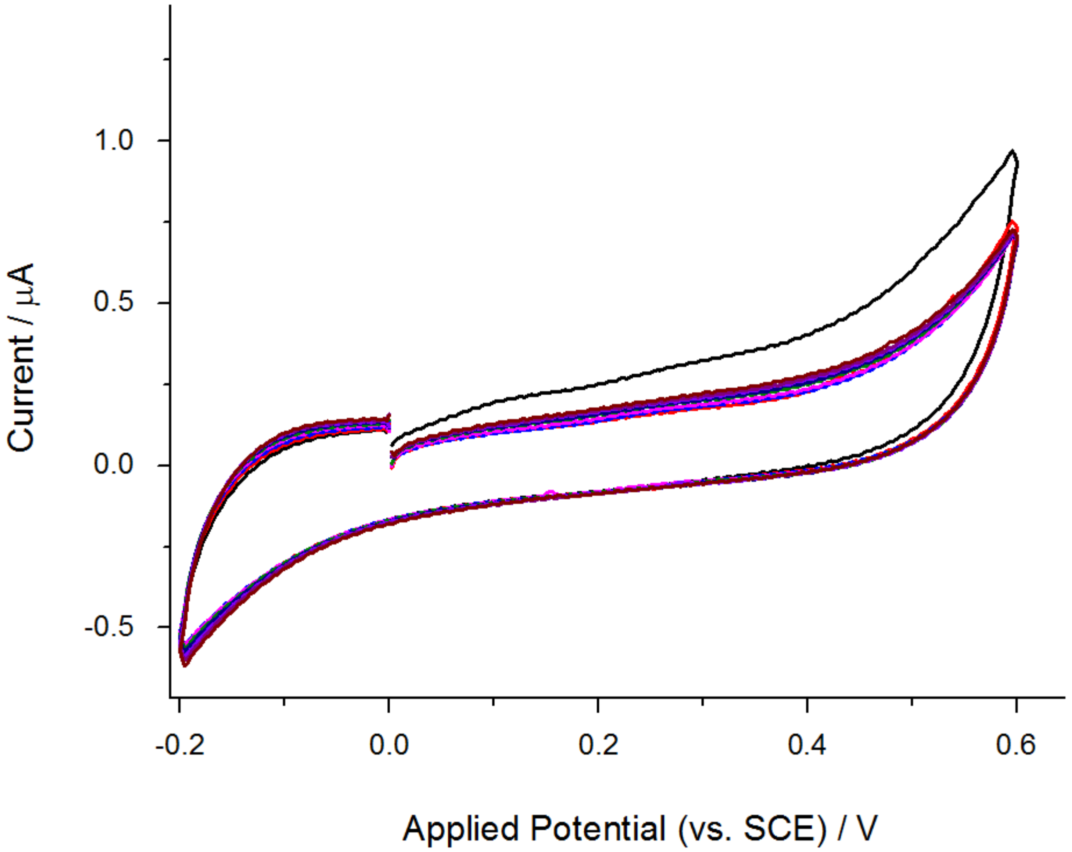

Fig. SI-6: The variation of the capacitative current with increasing immersion time in a deoxygenated BBS solution of pH 10.01 that contained 0.1 M KCl as the supporting electrolyte. These typical oxidative 100 mV s^{-1} voltammetric responses were recorded on the graphite/dioctyl phthalate paste, in the solution that the electrode was immersed in, at 298 K.