Supporting information

Synthesis and characterization of polyaniline, polypyrrole and zero-valent iron-based materials for the adsorptive and oxidative removal of bisphenol A from aqueous solution.

Lerato Hlekelele, Nomvuyo E. Nomadolo, Katlego Z. Setshedi, Lethula E. Mofokeng, Avashnee Chetty, and Vongani P. Chauke *

Polymers and Composites, Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa
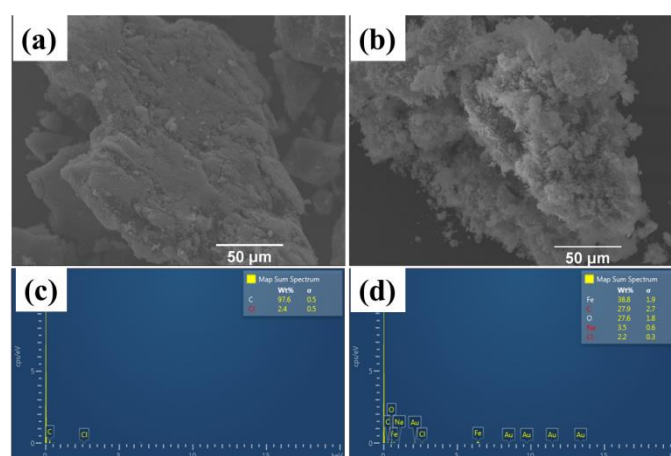
*VChauke@csir.co.za

(S1)

Fig. S1 SEM images (at 500x magnification) of **(a)** PPY/PANI and **(b)** Fe^0-PPY/PANI and EDS spectrum of **(c)** PPY/PANI and **(d)** Fe^0-PPY/PANI
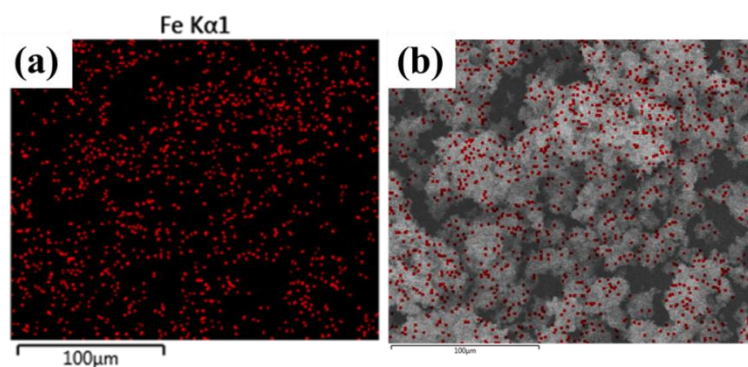
(S2)

Fig. S2 (a) EDS mapping of Fe and **(b)** a layered image showing the distribution of Fe^0 nanoparticles on the surface of PPY
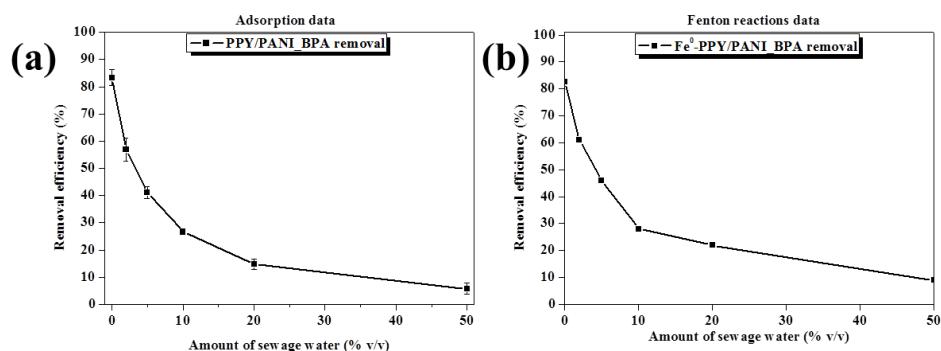
(S3)

Fig. S3. The removal efficiency of BPA in the presence of various concentrations of sewage water by (**a**) adsorption using PPY/PANI and (**b**) Fenton-reaction using Fe^0-PPY-PANI. Experimental conditions: 200 ml of 50 ppm BPA, pH 6 for adsorption experiments and pH 3 for Fenton reactions and 100 mg of adsorbent or Fenton catalyst and 15 ppm H_2O_2 for only Fenton reaction.
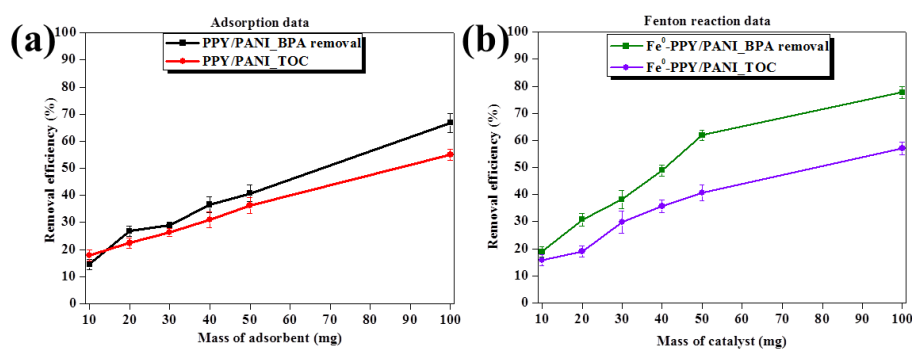
(S4)

Fig. S4. Effect of the mass of (**a**) adsorbent and (**b**) Fenton catalyst on the removal of BPA and total organic content. Experimental conditions: 200 ml of 50 ppm BPA, pH 6 for adsorption experiments and pH 3 for Fenton reactions and 25 % sewage-water.
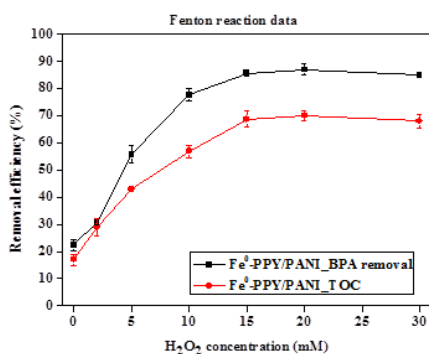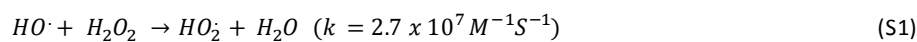
(S5)

Fig. S5. The effect that the concentration of H_2O_2 had on the removal efficiency of BPA and TOC by Fenton reaction using Fe^0-PPY/PANI.

(S6)

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (k = 2.7 \; x \; 10^7 \, M^{-1} S^{-1})$$ (S1)

$$HO_2^{\cdot} \rightarrow O_2^{\cdot-} + H^+$$ (S2)

(S7)

Table S1 Thermodynamic parameters that describe the adsorption of BPA onto PPY/PANI

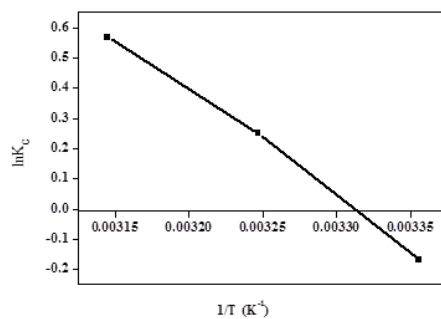| t (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})
298	0.418	−3.50	0.012
308	-0.640		
318	-1.50		

(S8)

Fig. S6 Plot of lnKc vs 1/T for the estimation of the thermodynamic parameters for the adsorption of BPA onto PPY/PANI.
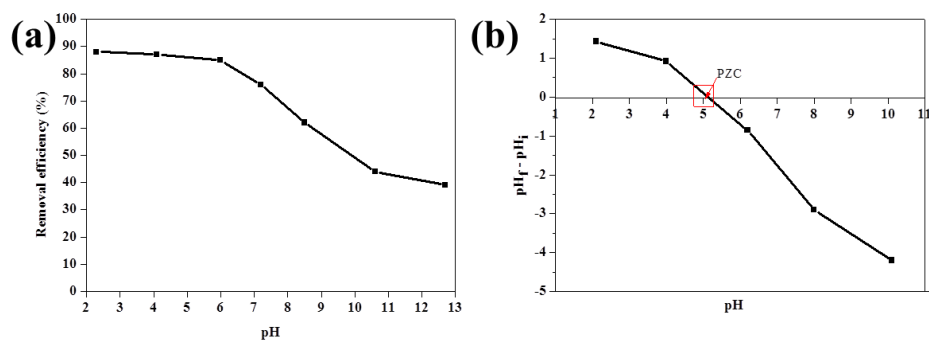
(S9)

Fig. S7 (a) Effect of pH on the adsorption of BPA onto PPY/PANI and **(b)** plot of pH point of zero charge of PPY/PANI.
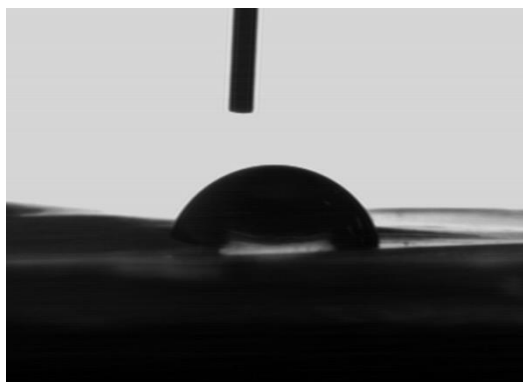
(**S10**)

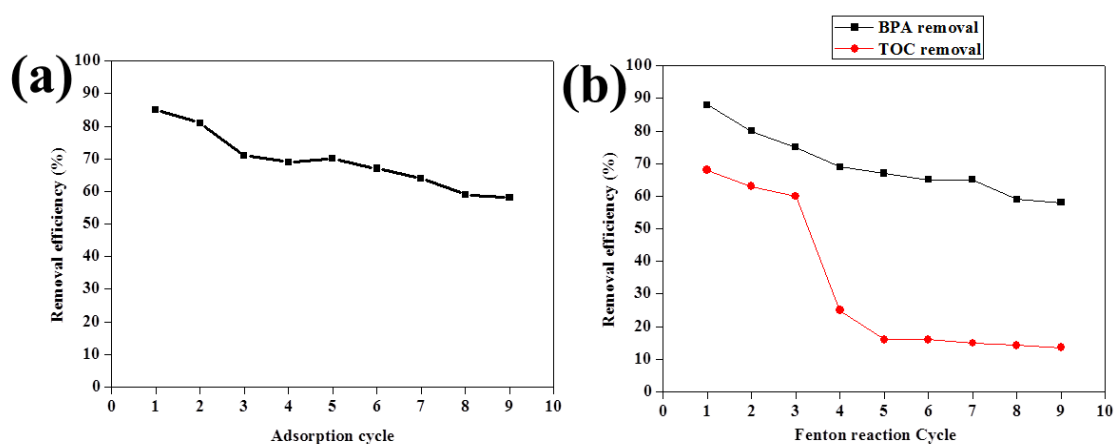**Fig. S8** representative image of a water droplet (pH 6) on PPY/PANI powder.

(**S11**)

Fig. S9 The removal efficiency of BPA using (**a**) PPY/PANI as an adsorbent and (**b**) Fe^0-PPY/PANI as a catalyst for the activation of 15 ppm H_2O_2. Experimental conditions: 200 ml of 50 ppm BPA, pH 6 for adsorption experiments and pH 3 for Fenton reactions, 100 mg of adsorbent or Fenton catalyst.

The recyclability of PPY/PANI as an adsorbent and Fe^0-PPY/PANI as a Fenton reaction catalyst were investigated by using the material over 9 cycles (**Fig. S7**). The adsorbent, PPY/PANI was regenerated after every adsorption by filtering off the remaining BPA solution from the previous experiment, drying the material at 80 °C overnight followed by washing the material with methanol (desorbing BPA from the material with methanol). The desorption of BPA from PPY/PANI was done by putting the material in 50 ml methanol followed by shaking the suspension for 48 hours on an orbital shaker. The removal efficiency of PPY/PANI decreased slightly over 9 cycles (**Fig. S9a**). On the 9th cycle, the removal efficiency was only 32 % less than the removal efficiency that was absorbed on the 1st cycle.

A different regeneration process was used for the regeneration of Fe^0-PPY/PANI. Here, after each BPA removal experiment, the remaining BPA solution was filtered off and the catalyst was dried at 80 °C in a vacuum oven. The dried catalyst was then dispersed in a 0.75 M methanolic $NaBH_4$ solution. This solution was shaken on an orbital shaker whilst being bubbled using a slow flowing stream of nitrogen gas. Here, it was also observed that the removal efficiency of the material remained high over 9 cycles (**Fig. S9b**). It was found that the removal efficiency decreased from 88 % to 58 by the 9th cycle. A different behavior was observed when studying the TOC removal efficiency. It was observed that the TOC efficiency decreased slightly between the 1st and 3rd cycle followed by a drastic drop in efficiency on the 4th cycle which remained constant until the 9th cycle. This happened because Fe^0 was being slowly leached from the composite between the 1st and the 3rd cycle and most of it was lost by the 4th cycle. Therefore, from the 4th cycle, the material behaved as an adsorbent rather than a Fenton reaction catalyst hence the relatively high BPA removal efficiency but the low mineralization efficiency.