

Functionalized Pyrolytic Carbon from Recycled Tyres: A Hybrid Material for Selective Removal of Pb, Cd from Waste Waters

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ABSTRACT

Carbon-based materials from recycled tyres (**PCox**) have been functionalized by covalently grafting organosilane functionalities (**Si-L**) bearing ligating groups **L** [where **L**=4-imidazolidithiocarboxylic acid or 4-imidazolcarboxaldehyde]. These ligands **L** bear with high affinity for heavy metals. Here Pb^{2+} , Cd^{2+} uptake was studied by Adsorption isotherms and pH-edge data using Anodic Stripping Voltammetry (ASV). The maximum metal-uptake capacity of **L@PCox** material is 32.3 mg of Cd^{2+} per gram of **L@PCox** when **L**=4-Imid-ald (47.4 mg/gr when **L**=4-Imid-dithio) at pH 7.0. For Pb^{2+} , the max uptake is 17.1mg/g (for **L**=4-Imid-ald) and 34.2mg/g when **L**=4-Imid-dithio at pH 7. In the presence of competitive Zn^{2+} or Cu^{2+} ions, the **L@PCox** materials show a strong selectivity for the Pb^{2+} or Cd^{2+} ions. This is attributed to the selectivity of the ligands **L** to the bigger lead or cadmium ions. When compared with the no functionalized pyrolytic carbon, the functionalised materials **L@PCox** show > 400% improvement for Cd and Pb uptake.

Keywords: pyrolytic carbon, functionalisation, Cd, Pb, metal uptake

INTRODUCTION

Pyrolytic char is one of the main products obtained after the pyrolysis process for disposing of waste tyres. It has contiguous structure with carbon black and this confers on it the general properties of carbonaceous materials such as thermal stability, high corrosion resistance in acid/base and low cost [1]. Concerning different technologies applied to the removal of heavy metal ions from aqueous bodies, metal adsorption onto solid supports such as activated carbon, zeolites, clays and metal oxides has been used so far [2]. However, the efficiency and selectivity of these solid supports are quite low, and improved metal absorbents have been prepared by coupling chelating ligands to support matrixes. The organic functionalities typically serve to form complexes with heavy metal ions, and the solid support allows easy removal from the liquid waste e.g. by filtration for example [3]. Various functionalized adsorbents with heavy metal complexing ligands have been reported [4,5] based mainly on polymers [6,7], clays [8,9], silica gel [3,10] and mesoporous silica [11,12]. Here, we report the functionalization of carbon-based materials from recycled tyres (**PC=Pyrolytic arbon**) *via* covalently grafting of organosilane-functionalities (**Si-L**) which bear ligating groups (**L**) with high affinity for heavy metals such as Pb²⁺, Cd²⁺. The so-prepared **L@PCox** hybrids contained functional groups L=4-imidazoledithiocarboxylic acid and 4-Imidazolcarboxaldehyde that are known to have specific ligation affinity for the heavy metals tested. Heavy-meta uptake was studied in aqueous solutions at pH 4-9 i.e. pertinent for industrial or surface waste waters.

METHODOLOGY

Oxidation of pyrolytic carbon. 5 gr of pyrolytic carbon (**PC**) were refluxed with 90 ml 65% v/v HNO₃ for 6h. The oxidized pyrolytic carbon (**PCox**) obtained was separated by filtration, washed exhaustively with distilled water until pH~7 and dried under reduced pressure at 40 °C for 12 h. DRIFTS-IR (cm⁻¹, selected peaks): 2919, 2855: ν(C-H); 1701: ν(C=O); 1542: ν(C=C); 1162: ν(C-O). Thermal analysis: the derivative thermogram of **PCox** shows a broad peak in the range of 130-420 °C assigned to the decomposition of -COOH surface groups with a 10.0 % weight loss and an intense peak at 600 °C assigned to the combustion of carbon support. The -COOH groups formed are *ca.* 2.2 mmol g⁻¹ determined by thermogravimetric and elemental analysis. The **PCox** had an average surface area of *ca.* 687 m² g⁻¹.

Synthesis of Organosilane-ligands. (a) *Synthesis of organo-silanes 4-Imid-dithio-OS and 4-Imid-ald-OS.* 1.5 mmol of 4-imidazoledithiocarboxylic acid or 4-imidazolcarboxaldehyde and 1.0 mmol of (3-glycidyloxypropyl)-trimethoxysilane or (3-aminopropyl)-trimethoxysilane respectively were stirred for 24 h in 10 ml of MeOH under N₂ at 60°C in order to generate **L1-OS** and **L2-OS** silane-precursors. (b) *Formation of modified carbon materials.* The **L1@PCox** and **L2@PCox** materials were prepared through co-condensation of **4-Imid-dithio-OS** or **4-Imid-ald-OS** precursors with the -OH functional groups of oxidised carbon **PCox**. Accordingly, 0.5 g oxidised carbon **PCox** and 5 ml EtOH were added to the precursor **L1-OS** or **L2-OS** solution, and the resulting slurry was stirred at 60 °C for 24 h. The obtained solids, **4-Imid-dithio@PCox** and **4-Imid-ald@PCox**, were washed several times with MeOH and EtOH and dried under vacuum at 60 °C for 12 h.

4-Imid-dithio@PCox: DRIFTS-IR (cm⁻¹, selected peaks): 2918, 2853: ν(C-H); 1702: ν(C=O); 1652: ν(C=N); 1561: ν(N-H); 1542: ν(C=C); 1159: ν(C-S); 901: ν(C-O-Si). Thermal analysis provides a weight

loss of 14.1 % assigned to the decomposition of the surface –COOH groups and the anchored organic ligand. This material showed an average surface area of *ca.* 45 m² g⁻¹.

4-Imid-ald@PCox: DRIFTS-IR (cm⁻¹, selected peaks): 2923, 2855: ν (C-H); 1702: ν (C=O); 1597: ν (C=N); 1542: ν (C=C); 1107: ν (C-O); 799: ν (C-O-Si). Thermal analysis shows a weight loss of 15.1 % corresponds to the decomposition of the surface –COOH groups and the anchored organic ligand. This material had an average surface area of *ca.* 75 m² g⁻¹.

Analytical determination of Cd²⁺ and Pb²⁺: Determination of metal concentrations in aqueous phase was carried out by Anodic Stripping Voltammetry using a Trace Master5-MD150 polarograph by Radiometer Analytica as described earlier [3]. The measuring cells were borosilicate glass cell from Radiometer. The working electrode was a hanging mercury drop electrode (HMDE), with an Hg drop with 0.4mm diameter generated by a 70 μ m capillary. The reference electrode was an Ag/AgCl electrode with a double liquid junction. The counter electrode was a Pt electrode. Initially, before the stripping step N₂ gas (99.999% purity) was passed from the measuring solutions to remove any trace O₂. During this step the solution was under continuous stirring at 525rpm. During the stripping step the solution was not stirred. Square Wave (SW) measurements were performed in the anodic direction i.e. Square Wave Anodic Stripping Voltammetry (SW-ASV), to quantify metal ions. Typically under our experimental conditions, 1.05 10⁻⁶M Pb(NO₃)₂ in 0.01M KNO₃ resulted in a current of I_p=0.851 μ A, E_p=-340mV at pH 6.5 and 1.05 10⁻⁶M Cd(NO₃)₂ in 0.01M KNO₃ resulted in a current of I_p=0.820 μ A, E_p=-460mV at pH 6.5. Adsorption kinetics of cadmium and lead onto L@PCox, were performed for contact times ranging between 0 and 120 min at pH 7, L@PCox = 0.1 g L⁻¹ and Cd(NO₃)₂ or Pb(NO₃)₂=3 mg L⁻¹. In each experiment the supernatant was collected by centrifugation and then analyzed for cadmium and lead. Adsorption isotherms were recorded at pH 7 in the presence of Cd(NO₃)₂ and Pb(NO₃)₂ at concentrations between 10- 50 mg g⁻¹, and 10- 60 mg g⁻¹ respectively for 0.1 g L⁻¹ of L@PCox suspended in 50 mL buffer solution in polypropylene tubes. The initial pH values of buffers were adjusted using small volumes of 2.5 M HNO₃ or 2.5 M NaOH to the desired value. After metals addition, the suspension was allowed to equilibrate for 120 min at room temperature (25 °C \pm 0.2) for cadmium and lead, while agitated in a magnetic stirrer. After completion of the equilibration, the suspension was centrifuged at 5000 rpm for 10 min. The Cd²⁺ or Pb²⁺ concentration of the supernatant solution was analyzed by Square Wave Anodic Stripping Voltammetry (SW-ASV) as described above. In the competition experiments, Cu(NO₃)₂ or Zn(NO₃)₂ were added in the same reaction mixture together with lead or cadmium and determined using SW-ASV.

RESULTS AND DISCUSSION

Synthesis of the adsorbents

The methodology applied here for anchoring of chelating ligands onto pyrolytic carbon uses silylation reaction of silane-precursors, depicted in Figure 1. The key concept of the present method is, first, a reaction of bifunctional, commercially available, alkoxy-silanes with 4-imidazoledithiocarboxylic acid or 4-imidazolcarboxaldehyde producing **4-Imid-dithio-OS** and **4-**

Imid-ald-OS precursors which has the alkoxy-moiety intact, and, second, silylation reaction of the so obtained silane-precursors with the surfacial –OH groups of the oxidized pyrolytic carbon.

Overall, the present synthetic procedure involves: (i) oxidation of the pyrolytic carbon **PC** with concentrated HNO_3 ; (ii) derivatization of the 4-imidazoledithiocarboxylic acid or 4-imidazolcarboxaldehyde to form silane-compounds; and (iii) anchoring of the silane-precursors to the oxidised pyrolytic carbon **PCox**. Derivatization occurs *via* reaction of 4-imidazoledithiocarboxylic acid and 4-Imidazolcarboxaldehyde with (3-glycidyloxypropyl)- or (3-aminopropyl)-trimethoxysilane to generate **4-Imid-dithio-OS** and **4-Imid-ald-OS** silane-precursors respectively. The propyl-trimethoxysilane moieties of **4-Imid-dithio-OS** and **4-Imid-ald-OS** allows their covalent attachment on the oxidized pyrolytic carbon **PCox** surface via hydrolysis and co-condensation with the –OH functionalities of the **PCox** leading to the formation of **4-Imid-dithio@PCox** and **4-Imid-ald@PCox** hybrid materials respectively.

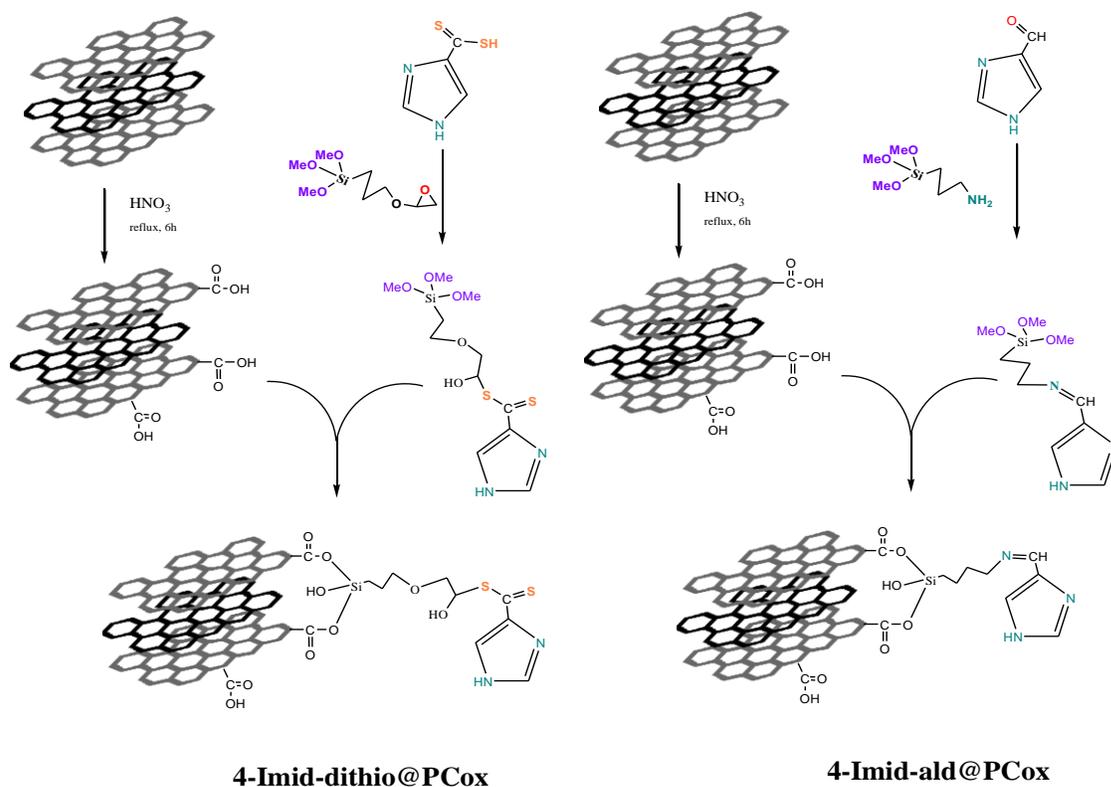


Figure 1 Grafting of 4-imidazoledithiocarboxylic acid and 4-Imidazolcarboxaldehyde on the surface of **PCox**

The DRIFTS-IR spectra of the **4-Imid-dithio@PCox** and **4-Imid-ald@PCox** show several bands corresponding to various structural units of the solid support as well as from the chelating ligands 4-imidazoledithiocarboxylic acid or 4-imidazolcarboxaldehyde. More specifically, the modified materials display the characteristic $-\text{CH}_2$ stretching bands in the region $2950\text{--}2850\text{ cm}^{-1}$ and $-\text{CH}_2-$ aliphatic deformation vibrations in the region $1500\text{--}1300\text{ cm}^{-1}$, as weak intensity bands. The bands at 1702 cm^{-1} are attributed to $\nu(\text{C}=\text{O})$ stretching vibrations. The $\text{C}=\text{N}$ and $\text{C}=\text{C}$ stretching vibrations of **4-Imid-dithio@PCox** were observed at 1652 and 1542 cm^{-1} , respectively. The same vibrations were also observed at 1597 and 1542 cm^{-1} attributed to imidazole ring in the **4-Imid-ald@PCox** material. The derivative thermograms for **4-Imid-dithio@PCox** and **4-Imid-ald@PCox** show 14.1 and 15.1% weight loss respectively, in the range $130\text{--}400\text{ }^\circ\text{C}$, which corresponds to a loss of anchored organic moieties and surface oxidised functionalities. Taking into account that the parent **PCox** material bears 10.0% [w:w] $-\text{COOH}$ surface groups which are decomposed in the same temperature region, the additional weight loss of 4.1 and 5.1% is assigned to the decomposition of the anchored organic ligand 4-imidazoledithiocarboxylic acid and 4-imidazolcarboxaldehyde respectively. The loading of 4-imidazoledithiocarboxylic acid and 4-imidazolcarboxaldehyde is *ca.* 0.3 and 0.5 mmol g^{-1} respectively.

Heavy Metal Uptake

Pb²⁺ uptake: Figure 2 presents the uptake of Pb^{2+} ions by 4-imid-ald@PCox (2A) or 4-imid-dithio@PCox (2B). The functionalised materials have significantly i.e. at least fourfold, improved Pd-uptake compared to the untreated pyrolytic carbon material (PC). Then pH-edge profiles in Figure 2 indicate that 4-imid-ald@PCox binds Pb via the imidazole group which deprotonates at alkaline pH. In contrast or 4-imid-dithio@PCox can bind metal cations at all the pH values tested. This is attributed to Sulfur atoms that have strong affinity for Cd and Pb. The S atoms act synergistically with the imidazole, thus achieving a higher Pd-uptake than imidazole alone.

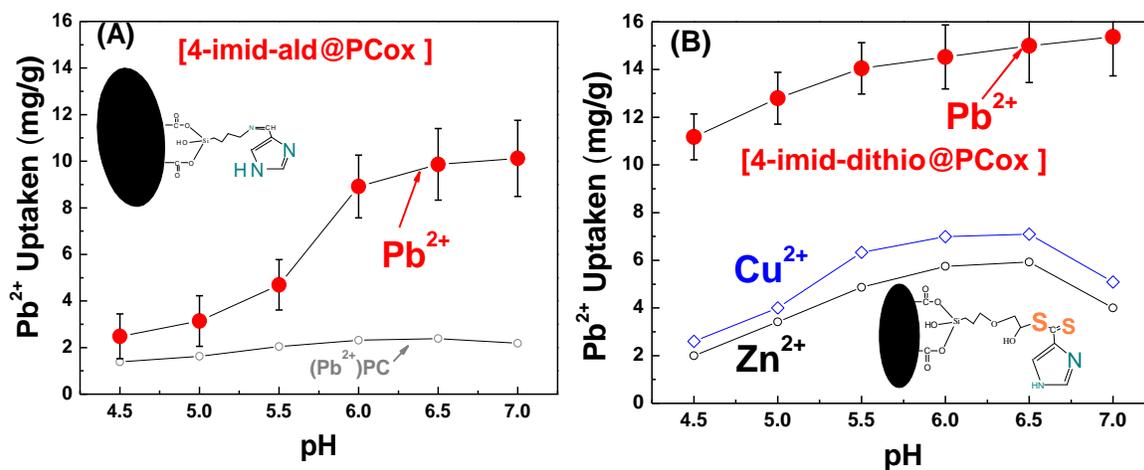


Figure 2 (A) Adsorption pH-edge for Pb^{2+} onto or 4-imid-ald@PCox (\bullet) or untreated Pyrolytic Carbon (PC) (\circ). (B) onto 4-imid-dithio@PCox (\blacklozenge). In 2B, the pH-edge adsorption of Cu^{2+} (\blacklozenge) or Zn^{2+} (\circ) ions is shown.

Cd²⁺ uptake: Figure 3 presents the uptake of Cd²⁺ ions by 4-imid-ald@PCox (A) or 4-imid-dithio@PCox (B). As in the case of Pb, the functionalised materials have significantly better Cd-uptake ability, than the untreated pyrolytic carbon material (PC). The beneficial role of the S-atoms in or 4-imid-dithio@PCox is also seen in Figure 3B e.g. vs. imidazole alone, in 4-imid-ald@PCox Figure 3B.

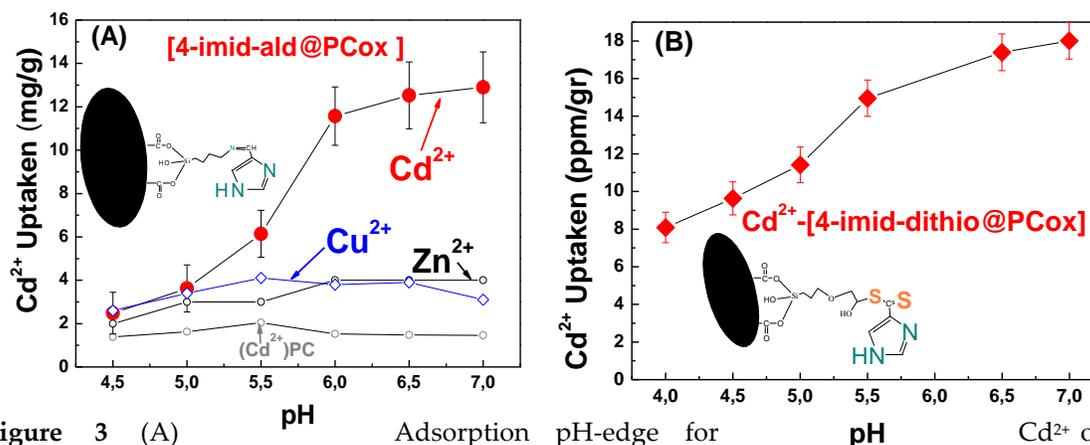


Figure 3 (A) Adsorption pH-edge for Cd²⁺ onto 4-imid-ald@PCox (•) or untreated Pyrolytic Carbon (PC) (◦). (B) onto 4-imid-dithio@PCox (♦),(◆). In 3A, the pH-edge adsorption of Cu²⁺ (◇) or Zn²⁺ (◦) ions is shown.

As in the case of Pb-uptake, at pH 7, both materials show improved sorption capacities. This indicates the involvement of pH dependent surface groups in the mechanism of cadmium uptake. The origin of this phenomenon can be understood based on the Surface Complexation Model developed in our previous work [3] for analogous ligands grafted on SiO₂ [3]. According to this, the binding of Cd²⁺ and Pb²⁺ ions is determined by [i] their binding affinities towards the S-atoms and the imidazole in 4-imid-dithio while the imidazole is the only functional group in 4-imid-ald. On the other hand the high affinity of Pb for the S-atoms in 4-imid-dithio@PCox render this material stronger adsorbent for Pb-ions at all pH values. On the other hand imidazole has higher affinity for Cd binding than for Pb, thus the Cd-uptake by 4-imid-ald@PCox is higher for Cd than for Pb.

Competitive Metal Uptake: The data in Figure 2B, show that 4-imid-dithio@PCox has an almost 100% higher Pb-uptake affinity than for Cu²⁺, and ~130% higher affinity for Pb²⁺ vs. Zn²⁺. This is due to the high binding affinity of the imidazole/S unit for Pb²⁺ ions. Similarly, 4-imid-ald@PCox shows a significantly higher binding affinity for Cd²⁺ ions than for the Cu²⁺ or Zn²⁺ ions. In Table 1 we summarise the maximum metal uptake capacity for Cd²⁺ or Pb²⁺ when present simultaneously with Cu²⁺ or Zn²⁺ ions.

All experiments were performed at a neutral pH 7 for an initial metal concentration 50mg per gram of material. The binary-metal data, in Table 1 clearly exemplify the effect seen in the pH-edge data of Figures 2B and 3A. 4-imid-dithio@PCox shows a 4:1 to 2:1 selectivity for Cd over Cu or Zn respectively. 4-imid-ald@PCox shows a 4:1 and 3:1 for Cd²⁺ over Cu and Zn respectively. The higher affinity for the bigger (Cd²⁺, Pb²⁺) ions is attributed to a chelation effect originating from the 4-imid-ald/dithio ligands on the oxidized pyrolytic carbon matrix.

Table 1 Maximum Metal Uptake Capacity of the functionalized PCox materials at pH 7.0

Material	Metal single-sorbates (mg of metal uptaken per gr of material)		Metal Binary-sorbates (mg of metal uptaken per gr of material)			
	Cd ²⁺	Pb ²⁺	Cd ²⁺ (Cu ²⁺)	Cd ²⁺ (Zn ²⁺)	Pb ²⁺ (Cu ²⁺)	Pb ²⁺ (Zn ²⁺)
4-imid-dithio@PCox	32.3	30.1	29.4(5.8)	11.2(6.9)	23.0(4.6)	25.7(13.9)
4-imid-ald@PCox	47.4	27.2	36.2(9.4)	33.2(11.4)	26.1(8.7)	30.2(12.6)

Comparison with analogous metal-sorbents: the present pyrolytic carbon-based materials can be compared with other chars e.g. such as pyrolytic wood [13], biochar or activated carbon that have been used for Cd and Pb uptake [14-16]. The present materials achieve 30-40 mg of Pb uptaken per gram for an initial metal concentration 50mg/gr i.e. >70% metal uptake. Chars derived from several pyrolytic woods [13] achieved <5mg Pb per gram at initial Pb >100mg [see review in 13]. Activated carbon from *Phaseolus a. huls* tested from Pb, Zn, Cu, Cd as in the present case at pH 7 achieved metal uptakes of 6-16mg/gr [16]. No completion/selectivity data were reported. In [14] binary metal sorbates (Cd-Cu) were evaluated by activated carbon (Aldrich Darco-120), at very low initial concentrations (0.6mg/gr). Cd uptake was severely outcompeted by Cu which was >95%uptaken vs. <50% of the Cd [14]. Thus, the present functionalized PCox materials constitute an example of high performance/high selectivity materials for Cd, Pb uptake.

CONCLUSION

Covalent rafting of appropriate organic ligands on PCox may result in significant enhancement of metal uptake by the adsorbent, compared to untreated Pyrolytic Carbon. Noticeably, the immobilised multifunctional ligands such as 4-imid-dithio and 4-imid-ald, have exhibited high Cd and Pb uptake-capacity at acidic as well as at neutral pH values. The high binding affinities of the Pb and Cd ions for the S-atoms of 4-imid-dithio and the idazole ring respectively result in different pH-edge profiles for the two metals. The data show that the presence or absence of protonable groups on the ligand determines the pH-edge profile in combination with the hydrolysis profile of

the metal ion under study. Thus both the nature of the ligand as well as its surface concentration are of equal importance for the sorbing capacity of the material.

ACKNOWLEDGEMENTS

This research has been co-financed by the European Union (European Regional Development Fund – ERDF) and Greek national funds (EPAN-II), PEP–Sterea Ellada–Epirus–Thessaly within Action SYNERGASIA-2011.



Ε. Π. Ανταγωνιστικότητα και Επιχειρηματικότητα (ΕΠΑΝ ΙΙ), ΠΕΠ Μακεδονίας – Θράκης, ΠΕΠ

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