Processing of Iridium Doped Materials and Experimental Investigation of Their Hydrogen Adsorption Capacity

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The paper aims to present the investigation of H_2 adsorption capacity in metal doped nanostructured materials, by using two methods. Carbonic materials are considered to be one of the most promising materials to be used for hydrogen adsorption and storage. They have different applications and one of the most important is considered to be fuel cells technology. By using metals for doping these materials, the adsorption capacity increases, thus approaching the target of 6.5% weight ratio of H_2 adsorbed in a substrate. Within these investigations multi-wall nanotubes and poly-aniline have been used as substrates. The poly-aniline has been prepared and doped in laboratory while the nanotubes used in experiments have been purchased from the market and afterwards doped in laboratory. The doping procedure consists of a physical-chemical method which involves salts of the metal for doping and the use of ultrasounds in order to activate the substrate for doping. The adsorption capacity of the carbonic materials has been determined by using spill over phenomena in a PCT Pro-User apparatus, provided by SETARAM and also by cyclic voltametry, by using VoltaLab-40 apparatus. In order to investigate the adsorption capacity of the nanostructured carbonic materials, the experiments have been carried out at different pressures. Both substrates have been characterized in order to determine their porosity, BET surface and structure. The collected data have been processed by using the PCT Pro-User apparatus's software. The results have been compared with the available data from literature and a good consistency was found.

Keywords: Hydrogen adsorption, weight ratio, doped carbonic materials, poly-aniline, and carbon nanotubes

Interest of hydrogen as a fuel has grown dramatically since 1990. It can be made available on-board vehicles in containers of compressed or liquefied H_2, in metal hybrids, via chemical storage or by gas-on-solid adsorption. Gas-on-solid adsorption is an inherently safe and potentially high energy density hydrogen storage method that could be extremely energy efficient. Possible current approaches to vehicular hydrogen storage include: (i) physical storage via compression or liquefaction, (ii) chemical storage in irreversible hydrogen carriers, (iii) reversible metal and chemical hybrids and (iv) gas-on-solid adsorption [1]. The research carried out within the current paper refers to the hydrogen storage using gas-on-solid adsorption method. The solids used as substrates for hydrogen storage are carbonic materials: multi-wall nanotubes (MWNT) and poly-aniline (PANI). Generally, activated carbons are ineffective in storing hydrogen because only a small fraction of the pores in the typically wide pore size distribution are small enough to strongly interact with hydrogen molecules at room temperature and moderate pressures. Recently, new carbon nanostructured adsorbents have been produced (graphite nanofibres, single and multi-wall carbon nanotubes) [1].

It has been observed that the hydrogen storage capacity of nanostructured carbon materials can be enhanced by tailoring their surface properties and sample characteristics [2]. Current paper approaches the surface properties enhancement by using high frequency ultrasounds in order to induce structural fractures within the carbonic material. An alternate approach to increase the hydrogen storage capacity of carbon nanostructured materials is by doping them with metals [2]. In the present paper, the nanostructured carbonic materials have been doped with Ir. It is well known that Ir, as well as Pt and Ru,

is one of the most reactive metals that can be used for increasing the hydrogen storage capacity of a substrate. The increased hydrogen storage capacity of metal doped carbon materials is attributed to the initial hydrogen adsorption by metal nanoparticles which subsequently dissociate the hydrogen molecules and spill them over to carbon nanotubes [2].

PANI and MWNT are a unique type of conducting materials in which the charge delocalization can, in principle, offer multiple active sites on the polymer backbone for the adsorption and desorption of hydrogen, involving weakening of the H-H bond followed by "spill over" adsorption of this hydrogen onto the adjacent nano-fibrous network [3].

Experimental part
Method for obtaining Ir doped MWNT

The following experiment refers to the obtaining and characterization of nanostructured carbonic materials as Ir doped MWNT. Thus, equal quantities of MWNT and Iridium Chloride ($IrCl_3$) are used in order to obtain Ir doped MWNT using chemical reaction.

MWNT are previously functionalized and then treated with $IrCl_3$. The necessary quantity of MWNT is mixed with 50 cm^3 deionised water and then, by using an ultrasound cannon their structure was functionalized. The frequency of the ultrasounds emitted by the cannon is 70 kHz, high enough to fracture the structure of the nanotubes. Separately, in a Berzelius glass, $IrCl_3$ is dissolved in deionised water and heated at 80^0C. The dissolved substance is mixed with the functionalized MWNT and heated for an hour at 80^0C. In the next stage, the mixture of $IrCl_3$ and MWNT are ultra sounded using the ultrasound cannon. This intensive mixing ensures a better contact

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between MWNT and Ir ions. In a separate glass 3 cm³ of formic acid is diluted in 25 cm³ of deionised water and then it is poured on the IrCl₃ and MWNT mixture. This final mixture is heated at 80⁰C for an hour and after that is vacuum filtered. The obtained solid mixture is then washed until its pH reaches 7. The obtained doped nanotubes are then heated at 100⁰C in a vacuum drying chamber. The dopping procedure above described is also involved in synthesis of some carbon supported catalysts when the imprinting of precursor is on active carbon or on vegetal materials which is then pyrolized and activated [4,5].

Method for obtaining Ir doped PANI

PANI was prepared in the laboratory by chemical oxidation of aniline sulphate ($C_{12}H_{16}N_2O_4S$) 0.2M with ammonium peroxydisulfate (($NH_4)_2S_2O_8$) 0.2M according to the literature [6-8]. High purity $C_{12}H_{16}N_2O_4S$ and (($NH_4)_2S_2O_8$) have been dissolved in sulphuric acid (H_2SO_4). Both solutions, having the room temperature, were mixed by using a magnetic stirrer in order to allow the polymerization process to take place. The solution has been filtered and then washed with H_2SO_4 in order to remove the collateral compounds, the oxidant and the residue. In addition, acetone has been used to wash even deeper the precipitate. The resulted poly-aniline salt ($C_6H_5-NH-HSO_4$) has been heated for 3 hours at 70⁰C in a drying chamber. 500 mg of obtained poly-aniline has been dispersed in deionised water by using the ultrasound cannon above presented. Then, 1 g of sodium hydrogen carbonate has been added and the solution was boiled for 30 min. Meanwhile, IrCl₃ dissolved in deionised water has been added to the boiling solution and ultra sounded for 15 min. This final mixture was heated at 80⁰C for an hour and after that vacuum filtered. The obtained solid mixture is then washed until its pH reaches 7. The obtained doped poly-aniline was then heated at 100⁰C in a vacuum drying chamber.

Results and discussions
Characterization of the materials

Each obtained doped carbonic material has been characterized both structural and functional. Structural characterization has been done by: X-Ray diffraction and

BET analysis. Functional characterization has been done by cyclic voltametry and physical adsorption of Hydrogen in order to determine their adsorption capacity.

Structural characterization by X-Ray diffraction

The method is based on qualitative analysis of the crystalline phases within a polycrystalline material by using X-Ray diffraction. A D8Advance diffractometer that uses Cu anode and X-ray tube was used. The sample vas polished with the smallest size of the polishing powder and then was placed in the diffractometer for analysis. The diffractions were made for the carbonic substrate and for the Ir doped one.

In figure 1 are presented the diffraction plots for MWNT and Ir doped MWNT.

As it can be seen in figure 1, even tough, initially, only graphite shows crystalline phase, after doping using the chemical treatment, Ir is widely spread within the structure of the nanotubes and graphite phase drastically decreased.

In figure 2 are presented the diffraction plots for PANI and Ir doped PANI.

As it can be seen in figure 2, PANI does not present crystalline phases before doping, but after the chemical treatment, Ir creates within the structure very well individualised crystalline phases.

Both for MWNT and for PANI, crystalline Ir was added to their inner structure.

Structural characterization by BET analysis

The method is based on the measuring the total adsorbed gas quantity on the surface of porous materials. The material is held at a temperature below the critical temperature of the gas. During the analysis, the pressure is modified until equilibrium is reached. Thus, the adsorbed gas quantity at the equilibrium is given by the difference between the admitted gas quantity and the one necessary for filling the material's pores. The used apparatus was Autosorb-1 having a pressure range between 0.001 and 1 bar. Data acquisition system allows us to determine BET surface.

In figure 3 is presented the BET surface for MWNT and Ir doped MWNT.

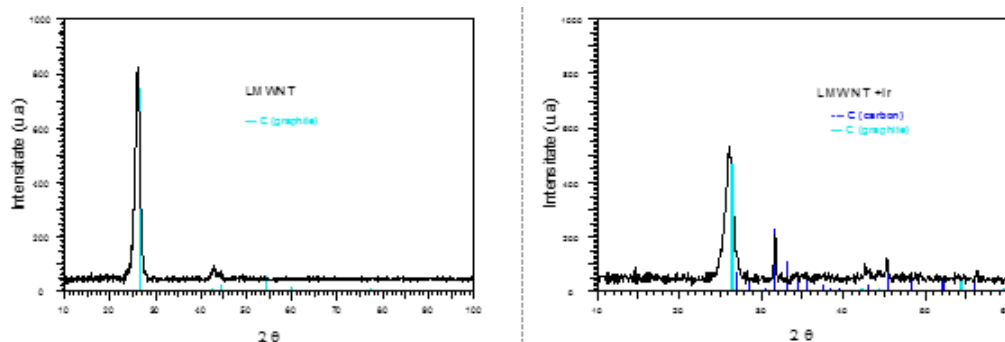In figure 4 is presented the BET surface for PANI and Ir doped PANI

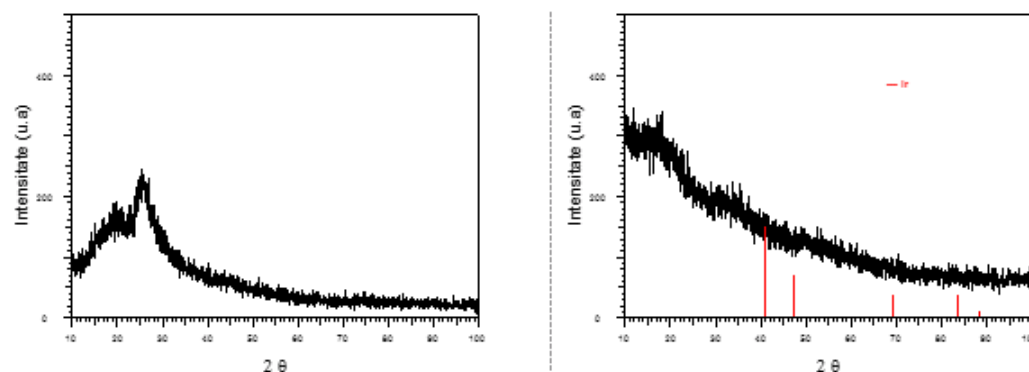Fig. 1. X-Ray diffraction for MWNT and doped MWNT

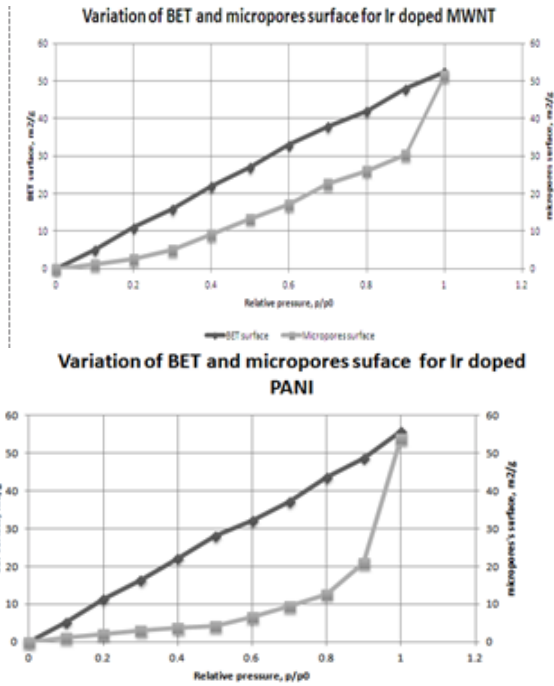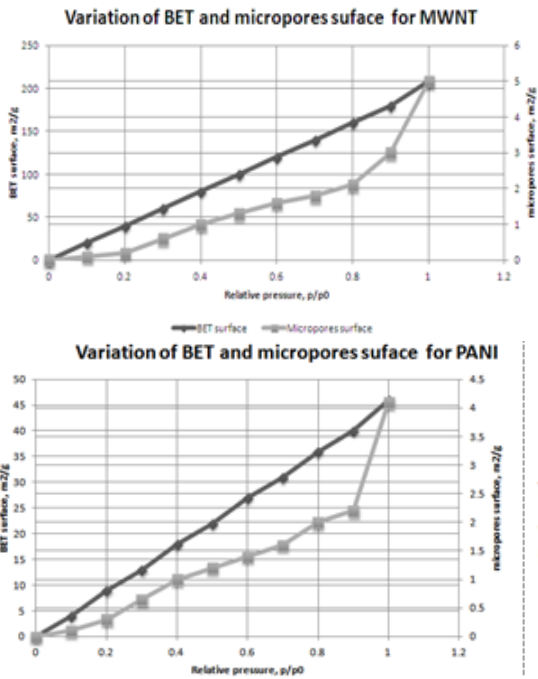Fig. 2. X-Ray diffraction for PANI and doped PANI

Fig. 3. BET surface for MWNT and doped MWNT

Fig. 4. BET surface for PANI and doped PANI

Functional characterization by cyclic voltametry

In order to determine the electrochemical activity of the materials, the active electrochemical surface has been determined by cyclic voltametry measurements which gives the ions transfer necessary to adsorb and desorbs hydrogen on the tested materials. Thus, the *total ions transfer* (Q_T) has been determined in the region of the adsorption/desorption potential, as it can be seen in figure 5. The method consists in applying a certain potential and monitoring the system's response in time. The apparatus used was *an all-in-one* radiometer analytical model VoltaLab-40 connected to a electrochemical cell type X51V00 having three electrodes. Q_T can be evaluated by using the following equation:

$$Q_T = \frac{1}{2v} \int_{E_i}^{E_1} (I_d - I_a) dE, \ [C/cm^2] \qquad (1)$$

where: v - sweeping speed [mV/s],
I_d -desorption specific current [mA],
I_a - adsorption specific current [mA],
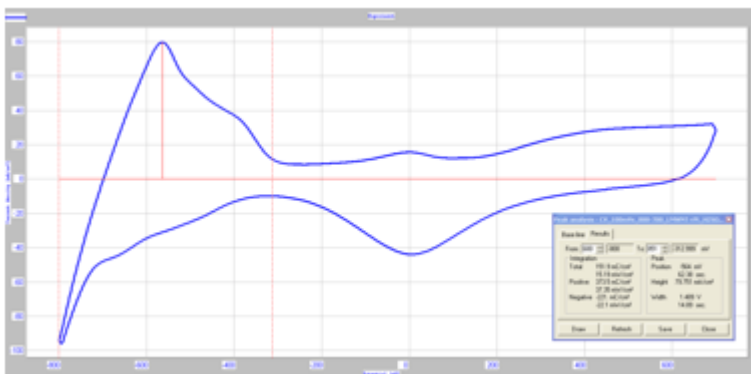E - Potential [mV].

Fig. 5. Example of how is calculated the total ions transfer Q_T
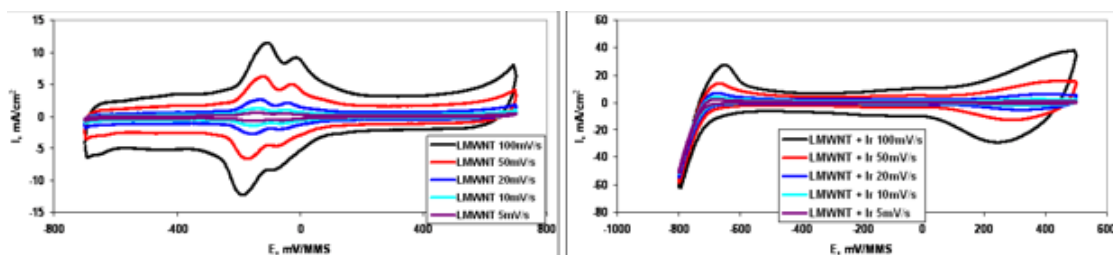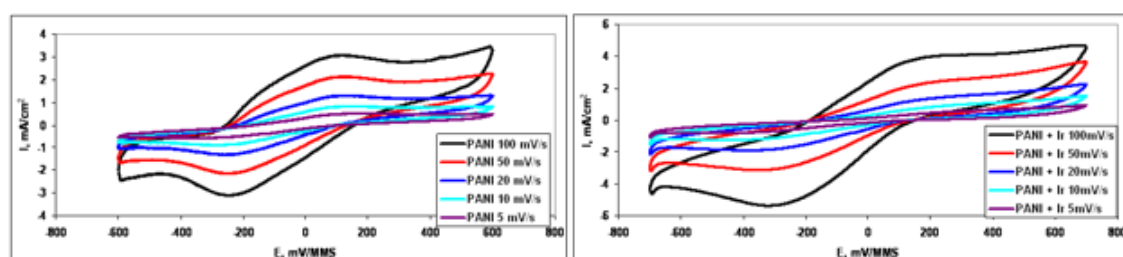

Fig. 6 Cyclic voltamograms for MWNT and doped MWNT

Fig. 7 Cyclic voltamograms for PANI and doped PANI

Sample	Qt, mC/cm^2	Electrical charges	H$_2$ ads, g/cm^2	H$_2$ ads, %
LMWNT 100mV/s	62.3	3.89E+17	6.46E-07	0.0162
LMWNT 50mV/s	65.1	4.06E+17	6.75E-07	0.0169
LMWNT 20mV/s	68.4	4.27E+17	7.09E-07	0.0177
LMWNT 10mV/s	70.7	4.41E+17	7.33E-07	0.0183
LMWNT + Ir 100mV/s	198	1.23E+18	2.05E-06	0.0514
LMWNT + Ir 50mV/s	205	1.28E+18	2.12E-06	0.0532
LMWNT + Ir 20mV/s	321	2.00E+18	3.33E-06	0.0833
LMWNT + Ir 10mV/s	490	3.06E+18	5.08E-06	0.1271
PANI 100mV/s	17.9	1.11E+17	1.85E-07	0.0046
PANI 50mV/s	25.2	1.57E+17	2.61E-07	0.0065
PANI 20mV/s	40.1	2.50E+17	4.16E-07	0.0104
PANI 10mV/s	58	3.62E+17	6.01E-07	0.0150
PANI + Ir 100mV/s	41.3	2.58E+17	4.28E-07	0.0107
PANI + Ir 50mV/s	48.4	3.02E+17	5.02E-07	0.0126
PANI + Ir 20mV/s	57.2	3.57E+17	5.93E-07	0.0148
PANI + Ir 10mV/s	96.8	6.05E+17	1.00E-06	0.0251

Table 1
OBTAINED CHARGES AT DIFFERENT ELECTRICAL POTENTIAL FOR DOPED MATERIALS

Table 1 summarize the results obtained during the cyclic voltametry testing of the materials.

Functional characterization by physical adsorption of hydrogen

In order to determine the hydrogen adsorption capacity of the nanostructured carbonic materials, the following method has been used. The material has been put in a tight closed recipient and pressurised hydrogen has been inserted. The pressure has been kept constant until the equilibrium has been reached. Then, a new increase of the pressure took place, and so on until the final pressure and equilibrium were reached. The used apparatus was a PCT Pro-user delivered by Setaram. The experiments have been conducted at three different pressures, 10, 20 and 30 bars. The results have been plotted as mass ratio (wt. %) of adsorbed hydrogen vs. pressure.

The following figures show the comparative data between MWNT and PANI at similar pressures. Thus, figure 8 presents the registered data at 10 bars for MWNT.

Figure 9 presents the registered data at 20 bars for MWNT.

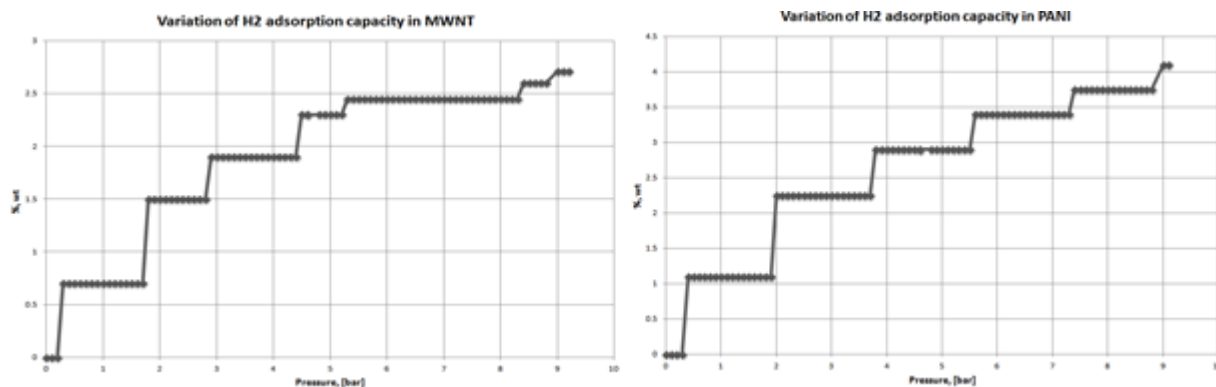Figure 10 presents the registered data at 30 bars for MWNT.

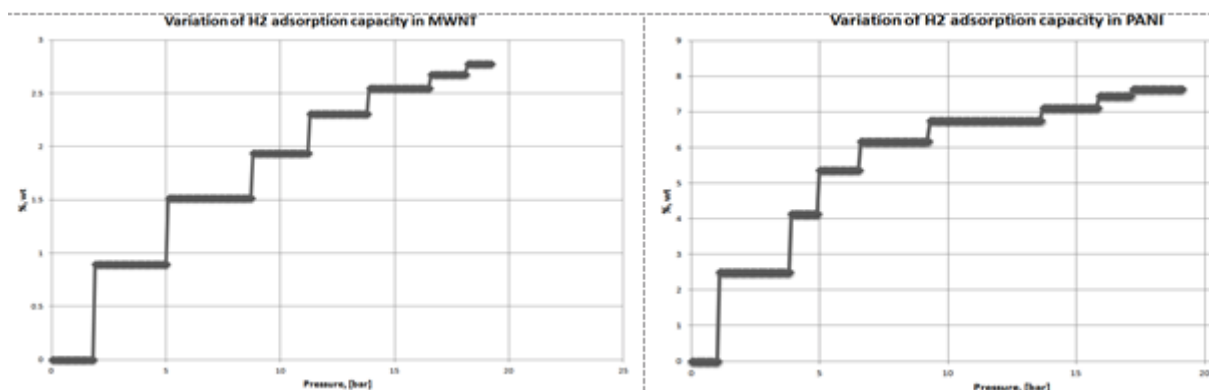Fig. 8. Wt% of hydrogen adsorption at 10 bar for MWNT and PANI

Fig. 9. Wt% of hydrogen adsorption at 20 bar for MWNT and PANI
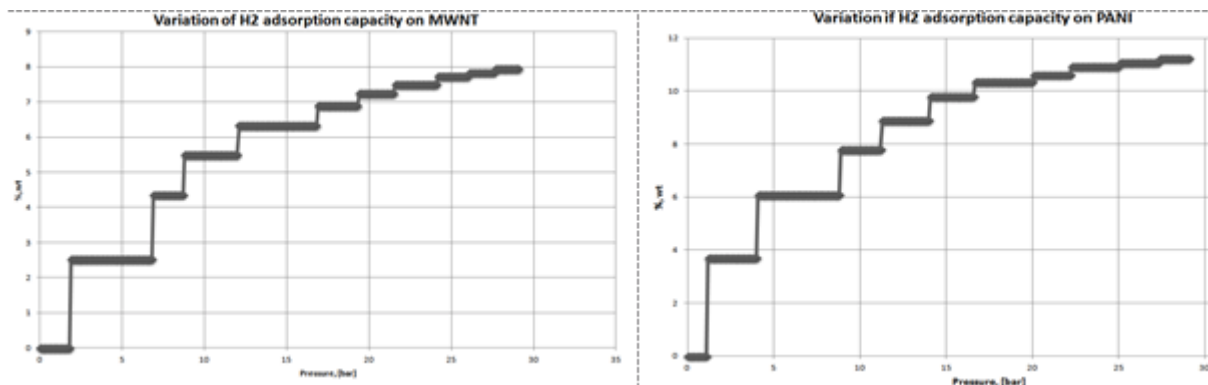
Fig. 10. Wt% of hydrogen adsorption at 30 bar for MWNT and PANI
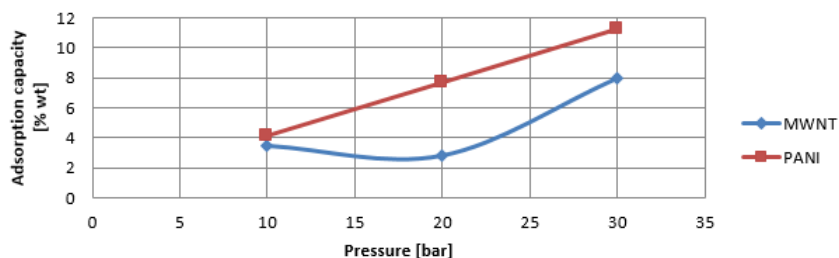

Fig. 11. Comparison between Ru doped MWNT's and PANI's adsorption capacity

Figure 11 shows a comparative analysis of the adsorption capacity of MWNT and PANI at different pressures.

Conclusions

By doping using Ir in its metal form, the specific surface modifies due to the fact that the metal chemically reduces when used as doping for nanostructured carbonic material. In the same time, the pores medium diameter increases along with the specific area of the pores. Thus an increase of almost three times can be observed for the specific area of the pores after the doping of the carbonic substrate.

After analyzing the data regarding the adsorption degree by using cyclic voltametry, it was determined the doping increases the material's action on the adsorption phenomena. Thus, the average adsorption degree of the doped material increases almost two and three times comparing with the un-doped one in the case of both materials.

After performing the experiments of physical gas-on-solid adsorption of hydrogen, it was determined the weight ratio of adsorbed hydrogen increases as the pressure increases until values that are accordingly to the ones reported in literature. Thus, at 30 bar, the weight ratio overpasses the set target by the US Department of Energy of 6.5 wt% [1], in the case of Multi wall nanotubes and approaches this target in the case of poly aniline event at lower pressures, 20 bar respectively.

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