EXPERIMENTAL RESEARCHES ON POLYPYRROLE RETENTION CAPACITY OF HEAVY METALS FROM WASTE WATERS

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Abstract: The paper aims to explain the properties of polypyrrole to retain some heavy metals from solutions. The objectives were to the following: experimental study of obtaining the nanostructured polypyrrole by chemical polymerization in the presence of Cl⁻; investigation of nanostructured polypyrrole by UV-Vis and IR spectroscopy, atomic force microscopy; investigation of polypyrrole ability to retain heavy metals from solutions by atomic absorption spectroscopy. The capture of heavy metals in solution, one can derive interesting compounds with photochemical properties where the heavy metals are captured of certain noble metals such as gold.

Keywords: polypyrrole, heavy metals, transition metals

1. INTRODUCTION

Pyrrole is a heterocyclic aromatic organic compound with five atoms ring and it has the formula C_4H_5N.

Pyrrole polymerization under specific conditions generates polypyrrole (PPy). In many articles discussing electropolymerization of polypyrrole and polypyrrole structures resulting properties [1, 3-8].

PPy has conducting properties and it is attractive for use as an absorbent due to its nitrogen hetero atom in the chemical structure and ion exchange property.

In this paper are presented few results on chemical polymerization of pyrrole in homogeneous solution. Polymerization may occur in the presence of various oxidants, the most common being ferric chloride.

Contamination with heavy metals from various technological operations is a major environmental problem. These metals have extremely high toxicity, even at low concentrations. For some heavy metals in waste waters, toxic levels of concentration may be just above the base naturally found in nature. If unrecognized or treated wrong, toxicity can cause significant illness and reduced quality of life.

The conventional methods for the extraction of heavy metals from waste waters include oxidation, reduction, precipitation, membrane filtration, ion exchange, electrochemical operations, biological treatment, and adsorption.

In addition to all available technologies, adsorption on solid substrate was used as one of the best methods of extraction of heavy metals from solutions. For the extraction of heavy metals, solid materials have been used: biomass, polymers, active carbon, and various clays.

Many studies have been conducted to evaluate the efficiency of compounds in contaminated water and soil remediation. The reaction mechanism for metal immobilization includes: an ion exchange process; surface complexation; precipitating a compound/ nanocomposite of metal retained; removing metal captured by substitution with another metal less damage during recrystallization.

Due to limited knowledge of the contribution of each metal extraction process, it seems that these mechanisms can be improved. Waste waters are multicomponent systems and competition between heavy metals extraction efficiency is reduced to heavy metals such solutions.

2. EXPERIMENTAL PART. RESULTS AND DISCUSSION

2.1. Equipments

The UV-Vis spectra have been obtained with a SPECORD M400 Carl Zeiss Jena spectrophotometer, with double beam and monochromator. The spectra have been recorded in the range 200-900 nm, in the cuvette with 1 cm optical length.

The FTIR spectra have been recorded by Attenuated Total Reflectance, ATR, with a Perkin Elmer Spectrum GX spectrometer (Perkin Elmer Ltd., UK), in the following conditions: range 4000 cm⁻¹ to 580 cm⁻¹, 32 scan, resolution 4 cm⁻¹

Images and AFM measurements were performed on four samples of PPy thin films by "tapping-mode", on a selected 500×500 nm area. With processing software

X'Pert from Pacific Nanotechnology, were determined average values (thickness of the polymer chains, their width chains) and selected the most representative topographic images.

AAS measurements have been achieved with an AVANTA spectrophotometer with hollow cathode lamp and by using a calibration curve for the analyzed elements.

2.2. Polypyrrole obtaining and polymerization study

At the beginning there was prepared an amount of 2,881 g solution (0.043 M) of pyrole in water witch was maintained at a temperature of 6 °C in an ice-water bath before the addition of ferric chloride (16.25 g). Basically, the polypyrolle was synthesized in water (50 ml) by mixing the pyrrol solution with the oxidizing ferric chloride solution (0.1 M).

Polymerization of pyrrole occurs through electron oxidation of polypyrrole to radical cation, which subsequently couples with another radical cation to form the bi-pyrrole. Then, this process is repeated to form a longer chain to the final form, a long conjugated backbone as seen in figure 1.
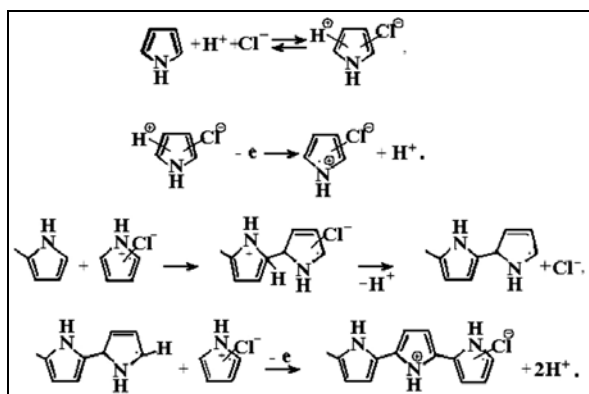

Fig. 1. The development of PPy chains [2]

Because this reaction is exothermic, adding ferric chloride had to be slow at low temperature. The synthesis of polypyrrole took about one hour without stirring. Pyrrole precipitate was collected by filtration followed by washing with distilled water and drying at 30 °C.

Polypyrrole obtained in a solution of ferric chloride was black with light blue reflection which is different from the colour of the black polypyrrole films, since those are not completely oxidized.

2.3. Spectrophotometer analyses of pyrrole polymerization

Figure 2 shows the characteristic absorption spectrum in the UV-Vis range of polypyrrole prepared by chemical oxidation.
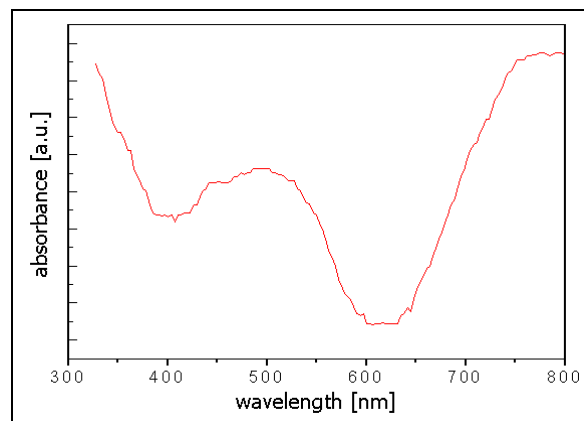

Fig. 2. UV-Vis absorption spectrum of polypyrrole doped with Cl⁻

At lower wavelengths (high energy) are noticed partially shaping the absorption band due to inter-band transitions, it shows that polypyrolle obtained has a relatively low doping degree.

The maximum absorption band due to transitions on the bipolaron is located at 492 nm (2.5 eV). Different structure of polypyrrole determines different values of the prohibited electronic band, which adjust the appropriate energy of electronic transitions on bipolaron levels.

Particularities of the molecular structure of polypyrrole nanostructures were investigated by IR spectroscopy. Sample preparation was as follows: PPy powder mixed with KBr and compressed formats those pellets.

Figure 3 represents the IR spectrum of the chemically prepared polypyrrole. The characteristic vibrational absorption bands of polypyrrole occur in the spectral range 500 - 1600 cm⁻¹: 902, 1035, 1177, 1300, 1454, 1545 cm⁻¹. This demonstrates that the molecular chains structure of polypyrrole is somewhat similar, and the differences in structure occur in mesoscopic scale.
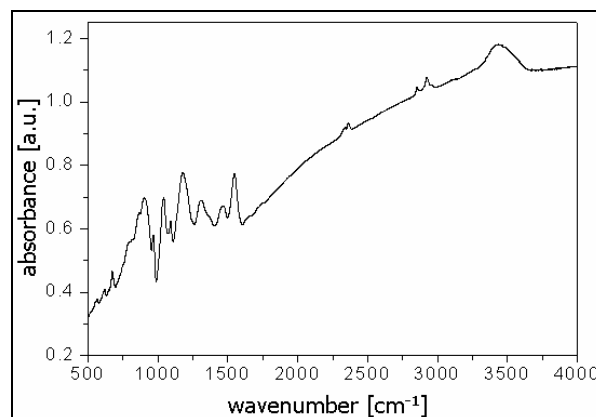

Fig. 3. IR spectrum of polypyrrole doped with Cl⁻

A characteristic band from the N-H vibration at 3430 cm⁻¹ in the PPy spectrum (Figure 3), it could not be seen at the spectrum of polypyrrole doped with the other ions. The appearance of the characteristic band

for N-H group can be related lower degree of oxidation of polypyrole.

2.4. Morphology studies on nanostructured polypyrrole by AFM

All the PPy film samples have the same roughness (r.m.s. = 0.2 to 0.24 nm). Comparing the images from Figure 4, the surfaces of samples 1 and 2 are rougher than the surfaces of samples 3 and 4.
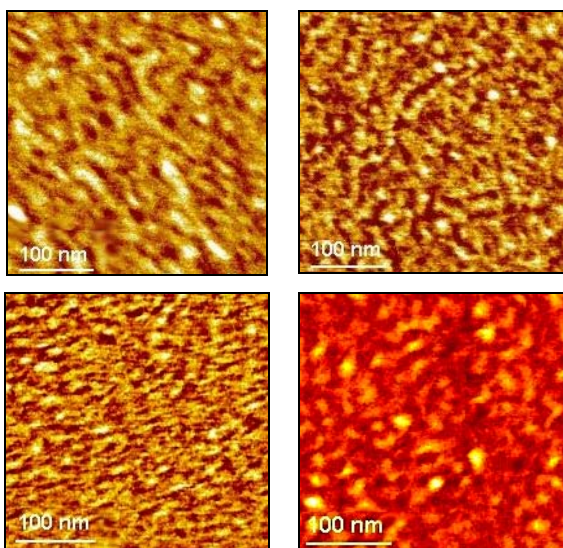

Fig. 4. **AFM images of PPy samples**

The brighter areas are PPy polymer chains. Field size (thickness) of polypyrrole chains is placed in the range 20 - 30 nm and the spaces between the polymer chains are in the range 5 - 10 nm.

2.5. Experimental study of interaction between some metal (Au, Sr, Pb) and nanostructured polypyrolle

The experiments on the retention of heavy metals in solution were performed using a nanostructured polypyrrole colloidal solution in water, neutral pH, and a ratio PPy/metal well established at 0.1 g of PPy per 25 ml metal solution.

After the polymer nanoparticles were added to the solution of heavy metal ions under constant stirring, samples of solution were taken at regular intervals (30 minutes) to determine the concentration of the remaining metals using atomic absorption spectroscopy.

AAS is an analytical method for quantitative determination of chemical elements employing the light absorption by free atoms in the gaseous state. This analytical method makes use of absorption spectrometry to assess the concentration of an analyte in a sample.

In order to analyze a sample for its atomic analyse, the sample should be atomized using flames or electro thermal atomizers. The atoms should be irradiated, and then, the radiation passes through a monochromator in order to filter the specific radiation for each element from any other radiation emitted by the source, which is finally measured by a detector.

Retention rate of metal by PPy was estimated by decrease the concentration of metal remained in solution, the concentration value determined by *atomic absorption measurements*.

2.5.1. Retention of gold

For the experimental study on retention of gold, an aqueous tetracloroauric acid solution ($HAuCl_4$) was used. Decreasing the concentration of gold is the presented in Figure 5.
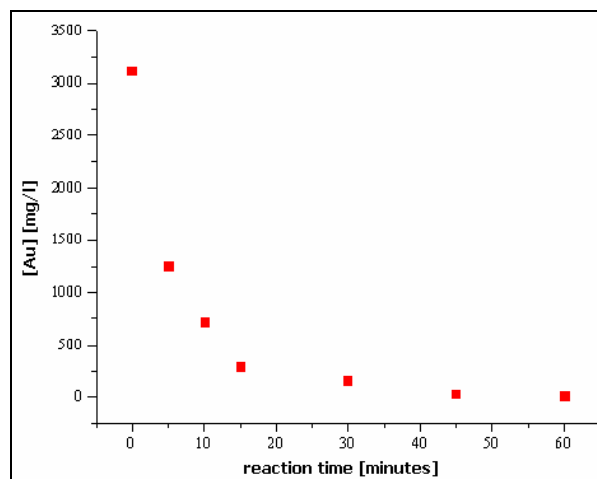

Fig. 5. The decrease in the concentration of gold, values determined by AAS
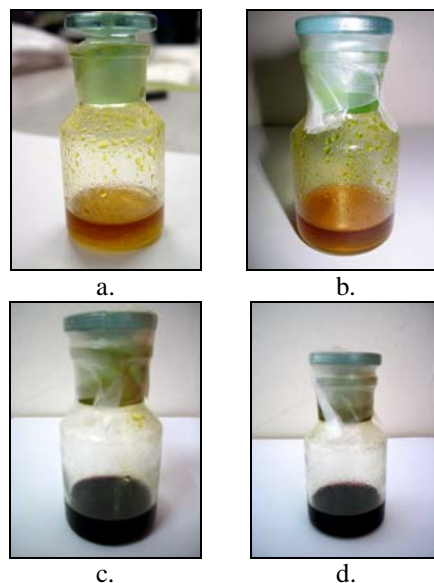

Fig. 6. The evolution of the retention phenomenon of gold in polypyrrole

There was a very rapid decrease in the first minutes of reaction, rapid decrease continued for 15 minutes of reaction. After this time, all values of gold concentration are about to zero, which is attributed to the gold saturation on the nanocomposites surface.

2.5.2. Retention of strontium

To study the retention of strontium was used an aqueous solution of strontium chloride ($SrCl_2$). Strontium concentration decrease is the presented in Figure 7.

It was noticed that the increasing concentration of strontium was held unlike a gold concentration decrease, progresively. After the first minute, the decrease was almost insignificant, followed 10 minutes after the start of reaction, the concentration decreased by approximately 60% from baseline.

After another 30 minutes, there was a dramatic decrease of approximately 90% of the initial value, entering concentration on a path of decline.
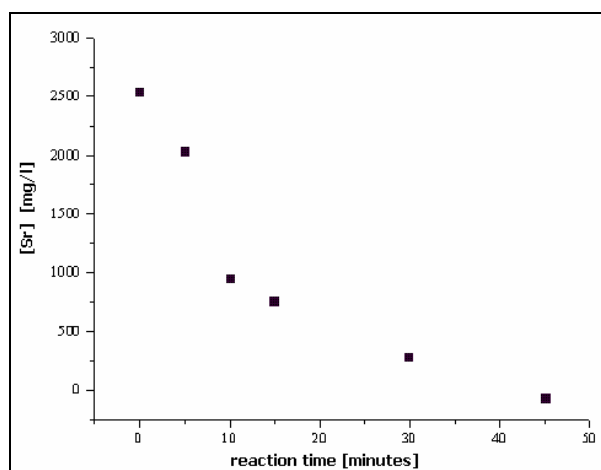

Fig. 7. The decrease in the concentration of strontium, values determined by AAS

It is noticed that retention rates of gold and strontium are similar but seem quite different mechanisms, which result from differences in retention occurred more during the reaction.

2.5.3. Retention of lead

It was tried on the lead, by using lead nitrate solution ($Pb(NO)_3$), but they are almost not retained of polypyrrole. The concentration of the lead solution was within measurement errors, as shown in Figure 8.
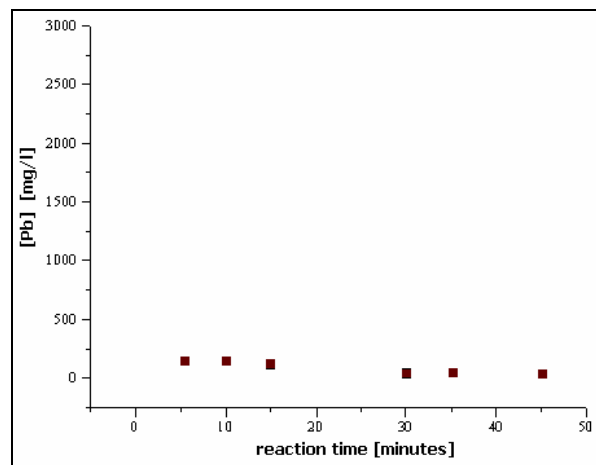

Fig. 8. The decrease in the concentration of lead, values determined by AAS

3. CONCLUSIONS

■ It was experimentally studied the polymerization of pyrrole (Py) by chemical methods in solution, using the chloride ion as a dopant.

■ Pyrrole polymerization was studied by absorption spectroscopy in the UV-Vis and IR spectroscopy.

■ The morphology was studied by AFM.

■ The polypyrrole doped with chlorine has a high specific surface area which can be used in order to retain heavy metals in solution. Speed potting determined by AAS depends significantly on the concentration of suspended PPy and PPy / metal.

■ The experimental results have shown that polypyrolle doped with chlorine ions represent a potential material used both for the recovery of noble metals (such as Au), and to reduce the concentration of heavy metals in different solutions and waste waters.

4. REFERENCES

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