STUDIES ABOUT DIRECTIONS OF RECOVERY THE WASTES FROM APPLE PROCESSING

STUDII PRIVIND DIRECȚIILE DE VALORIFICARE A DEŞEURILOR DE LA PROCESAREA MÃRULUI

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Abstract. *Agro-food processing industry provides appreciable amounts of waste, mostly biodegradable. Some of these are used effectively in obtaining various products for human or animal consumption, while others are used to extract various biological active components. Thus, waste material can be processed in anaerobic digestion for producing biogas, can be subjected to composting or worm composting processes in aerobic digestion or can be utilized as adsorptive material.*
Key words: *agro-industrial solid wastes, apple processing, direction of recovery*

Rezumat. *Industria de procesare a produselor agroalimentare este un furnizor de cantități apreciabile de deșeuri, în marea lor majoritate biodegradabile. O parte dintre acestea se utilizează eficient în obținerea de diferite produse destinate consumului uman sau animal, pentru extragerea diferitelor principii biologic active, ca material în procese de digestie anaerobă pentru obținerea de biogaz sau aerobă în procese de compostare sau viermi-compostare.*
Cuvinte cheie: *deșeuri agroalimentare solide, procesarea merelor, direcții de valorificare*

INTRODUCTION

Development of human society resulted not only in super-industrialization, but also in urban demographic explosion and, consequently, in generation of massive amounts of waste, mainly solid. Wastes, along with other sources of environmental pollution led to disruption of ecological balance of the environment. The specialists in environmental quality control have noted that even development of potential non-polluting economic sectors began to raise certain environmental pollution problems. Thus, the growth of agriculture and agro-food industry contributes to environmental pollution through waste generated by specific activities, as well as through the varied chemicals used in different amounts in order to improve the nutritional capacity of soil. To these, the effect of other chemical pollutants found in effluents that are discharged into the environment should also be considered (Suteu et al., 2009; Zaharia, 2010). Since the concept of sustainable development was introduced, solid waste issues became even more evident, considering that one cannot achieve sustainable development

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in economic, social and environmental protection without implementing a sustainable waste management (Zaharia and Suteu, 2011). Sustainable waste management include: (i) waste minimization, (ii) use of waste as secondary raw material, (iii) non-recoverable waste burial in landfills without affecting the environment and (iv) use of waste as alternative fuel (Suteu et al., 2009). After processing of agricultural raw materials can resulting sometimes large amounts of secondary products that unused properly can turn into waste. Large amounts of secondary products often result by processing of agricultural raw materials, which can turn into waste if are improperly used. In this context, scientists focus on the development of advanced processing technologies capable to reduce these by-products, but also of technologies that recover and convert them into useful products for human or animal consumption. A possibility to capitalize the agricultural by-products may consist in extraction of their active components that can be further used in cosmetics, pharmacy and nutrition (Horoba et al., 2001). It is also considered the possibility to integrate the waste resulted from different manufacturing stages into different biodegradation processes, such as anaerobic digestion (in order to produce biogas) or/and aerobic processes as composting or worm composting (Suteu et al., 2012a,b; Suteu et al., 2011). Agro-industrial wastes generated in different technological phases were tested as materials with adsorptive properties toward some chemical pollutants (metal ions, organic compounds) present in industrial effluents and domestic sewage, as a result of their composition in lignocellulosic compounds (Suteu et al., 2010; Suteu et.al., 2012a,b; Egila et al., 2011; Mahmoud et al.,2012).

This paper presents the results of a preliminary study concerning several possible directions of reusing the waste derived from apples processing.

MATERIAL AND METHOD

Materials. Preliminary experimental studies were carried out using biodegradable waste consisting in lignocellulosic material generated by industrial processing of several varieties of apples from Romania (Florina, Idared, Ionathan, Golden, Ionagold). Solutions of organic solvents (n-hexane and methanol), but also other common chemicals necessary for different purposes within the experimental studies were used as auxiliary materials. Stock solutions of dyes (Methylene Blue, Brilliant Red HE-3B, Rodhamine B) with concentrations of, respectively, 320 mg/L, 500 mg/L, and 479.2 mg/L, have been prepared by using bi-distilled water. The working solutions were obtained by appropriate dilution.

Methods. he components of apple wastes have been processed differently. A part of apple wastes was added to the mixture used in anaerobic and aerobic digestion processes (worms composting). The seeds have undergone extraction with solvent in a Soxhlet device type in order to obtain bioactive compounds or were tested in the view of their adsorptive potential for retention of textile dyes from aqueous media. Physico-chemical characterization of various materials was done by different techniques. These include (1) FT-IR spectroscopy involving a FT-IR BioRad spectrometer FTS2000 with 4 cm^{-1} resolution for 32 scans, using KBr pellets, and operating in wavelength range between 4000 to 400 cm^{-1}, (2) UV-Vis spectroscopy using a Jasco V550 UV-Vis spectrophotometer and (3) fluorescence spectroscopy through a PERKIN-ELMER fluorescence spectrometer. Adsorption studies were performed by batch method. An amount equal to 0.05 g of solid adsorbent was equilibrated with a volume of 25 mL of dye solutions by certain concentrations. Different pH values of initial solutions and also different temperatures have been employed within the study. After the equilibrium was reached, the dyes content in supernatant was determined spectrophotometrically. The adsorption efficiency of the solid waste was evaluated by determining the percentage of dye removal, R (%):

$$R=\frac{c_0-c}{c_0}.100 \quad (\%) \qquad (1)$$

where: c_0 and c are initial and, respectively, the equilibrium concentration of dye in solution (mg/ L).

RESULTS AND DISCUTIONS

Apples (*Malus domestica Rosaceae* family) are the fruits with the highest use due to their complex composition (Fig. 1), consisting in a big number of nutrients that meet almost all the needs of human body.

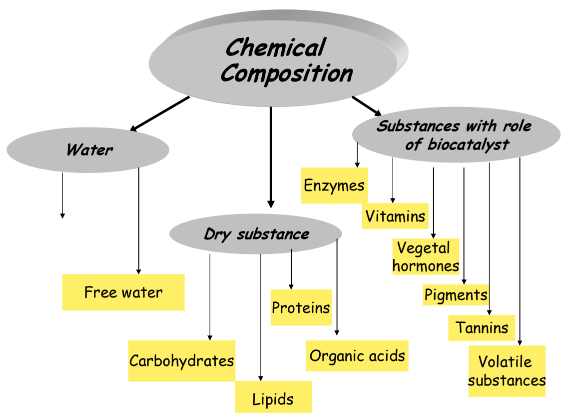


Fig.1 - Chemical composition of apples

The overall chemical composition of a fruit (with slight differences depending on variety) are : 84.5% water, 14.1% sugars, 0.2% pectic substances, 0.6% fats, 90 UI A vitamin, 0.02 mg % B2 vitamin, 0.1mg % B1 vitamin, 7mg% C vitamin, 7 mg% Ca, 10 mg% K, and small amounts of Al, Mn, S, Co, Fe, Zn, vitamins of group B (B5, B3, B6, B9), flavonoids and phenols (Maurice et al.1976). Apple seeds stand out by the presence of amygdalin (B17 vitamin), linoleic acid (48-64%), oleic acid (24-42%) and palmitic acid (48-71%). For this reason, apples are an important source of chemical compounds essential for a proper nutrition and processing of their waste can be a valuable source of biologically active substances. Apples waste, that include peels, seeds and spine may be fed in the mass of biodegradable waste in order to subject them to anaerobic digestion or to aerobic digestion (worm composting). In the first case, the apple waste are converted to biogas, while in the second, it become a source of nutrients and fibers essential for the development of micro- and macro-organisms involved in these biological processes (Suteu et al., 2012a,b; Suteu et al., 2011). Prior to processing, the apple seeds were dried and chopped. The material thus prepared was kept in closed containers. Extraction of bioactive compounds from apple seeds was achieved by the classical method of liquid-solid extraction using two solvents, n-hexane and methanol, both accepted by pharmaceutical, cosmetics and food industries. The results obtained from processing of spent material evidenced different selectivity for the two solvents used (fig.2).

Table 1

Conditions for extraction of bioactive compounds from apple seeds

Type of extraction solvent	n-hexane	methanol
Solid material for extraction (seeds) (g)	13.150	14.836
Volume of solvent extraction (mL)	160	160
Time of extraction (minute)	190 minutes	120 minutes

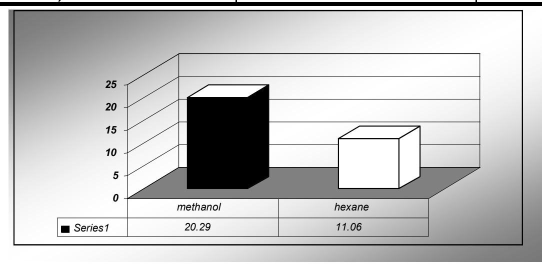


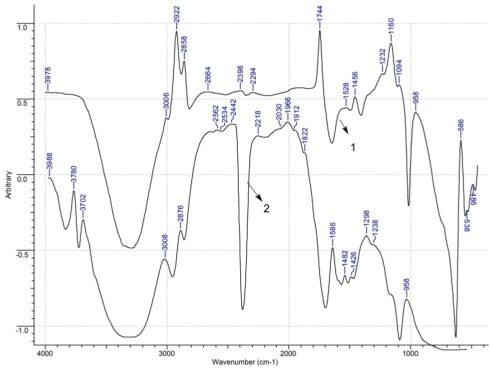
Fig. 2 - Percentage content of extracted substances

FTIR (fig.3a) *and UV-Vis* (fig.3b) *spectra* analysis shows the complex composition of both obtained extracted. Apart of evidencing the different selectivity of the two extraction solvents, the FTIR spectra (fig.3a) showed that besides various lipid fractions (represented by polycyclic unsaturated fatty acids, phospholipids, glycolipid etc., identified by the presence of characteristic groups - PO_2^- and R-O-P-O-R` [1200-1060 cm^{-1}], C=O [1500-1800 cm^{-1}], CH_2 [2700-300 cm^{-1}]) , there are also a number of other organic components (phytosterols, tocopherols, carotenoids, etc.), especially in the case of alcoholic extract. *UV-Vis spectra* (fig.3b) confirm the presence of phenolic and lipidic compounds, absorption limit being situated in the ranges 212-214 nm (lipidic compounds) and 275-290 nm respectively, attributed to phenolic compounds. Analysis of *fluorescence spectra* (fig.3c) confirms the different behavior of the two solvents used in extraction, one polar (methanol) and one non-polar (hexane). As demonstrated above have been extracted two categories of substances:

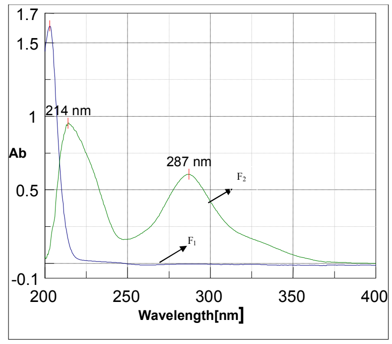
- in *methanol* phenolic compounds, characterized by absorption in UV-Vis at 287 nm wavelength (band characteristic to conjugated aromatic ring) and at 214 nm wavelength. This fact is revealed by fluorescence spectra (fig.3c) through characteristic fluorescence emission of aromatic structures (407.5 nm);
- in *hexane* the extraction of superior fat and aliphatic alcohols was achieved. One may observe only one adsorption band at 203 nm wavelength, without the involvement of double bonds or aromatic rings in the structure of separated compounds. This is revealed by the fluorescence spectrum (fig.3c) through

characteristic fluorescence emission of fatty acids and low molecular weight alcoholic structures (389 nm).

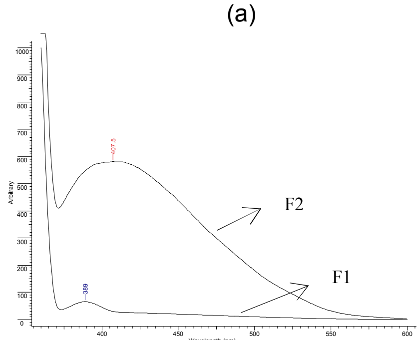
The results of the qualitative analysis of the two extracts is in agreement with some literature data (Lu and Foo, 1998), confirming the complex composition of apple and the possibility of using waste from their industrial processing as sources of biologically active compounds useful in pharmaceutical industry, food and cosmetics industries. Seeds, dried and chopped were used in adsorption experiments to retain some textile dyes present in aqueous and potentially present in industrial effluents.



(a)



(b)



(c)

Fig. 3 - (a) FTIR spectra of the extracted obtained in n-hexane (1) and methanol (2); (b) UV-Vis spectra of the extracted obtained in n-hexane (F1) and methanol (F2); (c) Fluorescence spectra (F1 - hexane si F2 - methanol)

Table 2

Characteristics and results of the dyes adsorption on apple seeds as adsorbent

Dye	Methylene Blue	Brilliant Red HE-3B	Rodhamine B
Operational characteristics			
Concentration of dye stock solution, mg/L	320	500	479,2
Concentration of dye working solution, mg/L	51,2	80	47,92
Molecular weight of dye, g/mol	320	1463	479
Solution pH	6	3	4
Temperature, ^{0}C	25	25	25
Work time, h	24	24	24
Adsorbent amount, g	0,05	0,05	0,05
Results of adsorption experimental works:			
Dye retention, %	64,4	86,75	14,98

Using aqueous solutions of three textile dyes and static adsorption method of separation were obtained results (Table 2) which certifies that this material can be a good and efficient adsorbent for this class of organic pollutant compounds.

Results were expressed as percentage retentions of textile dyes belonging to different structural classes (Brilliant Red HE-3B – reactive dye; Methylene Blue – phenotiazine dye; Rodhamine B – xantenic dye) and exhibited values ranged between 14.98 and 86.75 %. Along with the calculated adsorption capacities (about 3.3865- 26.73 mg/g), the values of percentage removal led to suggestion that the apple seeds can be used for removal of textile dyes from aqueous medium with good results (except Rhodamine), in the case of low flows.

CONCLUSIONS

1. The extract with bioactive compounds obtained from apple seeds using as solvent n-hexane and methanol were characterized with respect to their FTIR, UV-VIS and fluorescence spectra that led to identification of some lipid and phenolic fractions.

2. The adsorption studies of textile dyes on dry and chopped apple seeds highlighted a good adsorption capacity, with retentions of up to 26.73 mg/L and 86.75%, respectively.

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