Application of pectin and its compositions for heavy metals removal

Kostj Kozlov, Technologica LLC

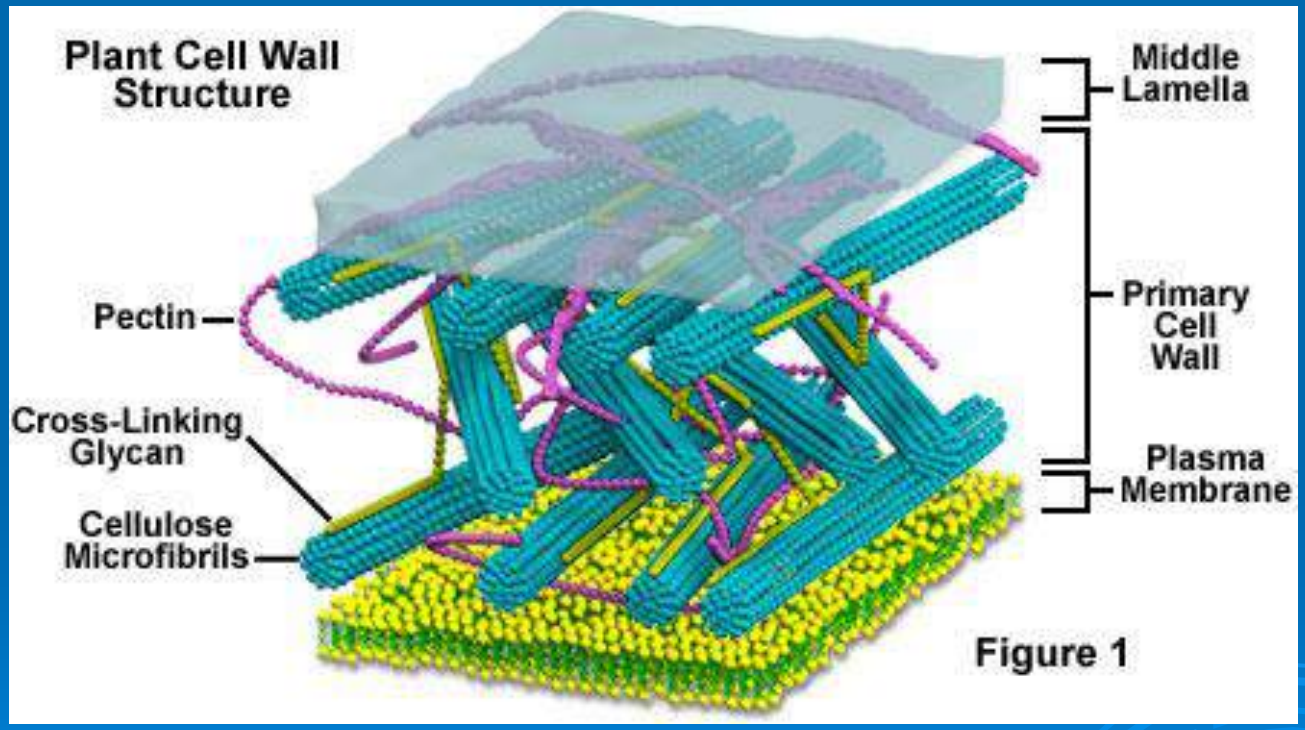
2ND NANOMED WORKSHOP
ADSORBENTS FOR REMOVAL OF HEAVY METALS.
CHARACTERISATION, PERSONAL CARE AND WATER TREATMENT
SCIENTIFIC PROGRAM

BUDAPEST, 4 December 2018

Functions of pectin

- plant growth, mechanical support, morphological development, fruit ripening, and emulsification of plant tissue;
- gelling and stabilizing polymer in diverse food and specialty products (thickener, water binder and stabilizer in beverages and dairy products);
- binds heavy metals by complexation – acts as natural cation exchanger in human diet;
- exhibit antioxidative, anti-hypertensive, cytoprotective, immunomodulatory, hypocholeste-rolemic, hypoglycemic, prebiotic activity

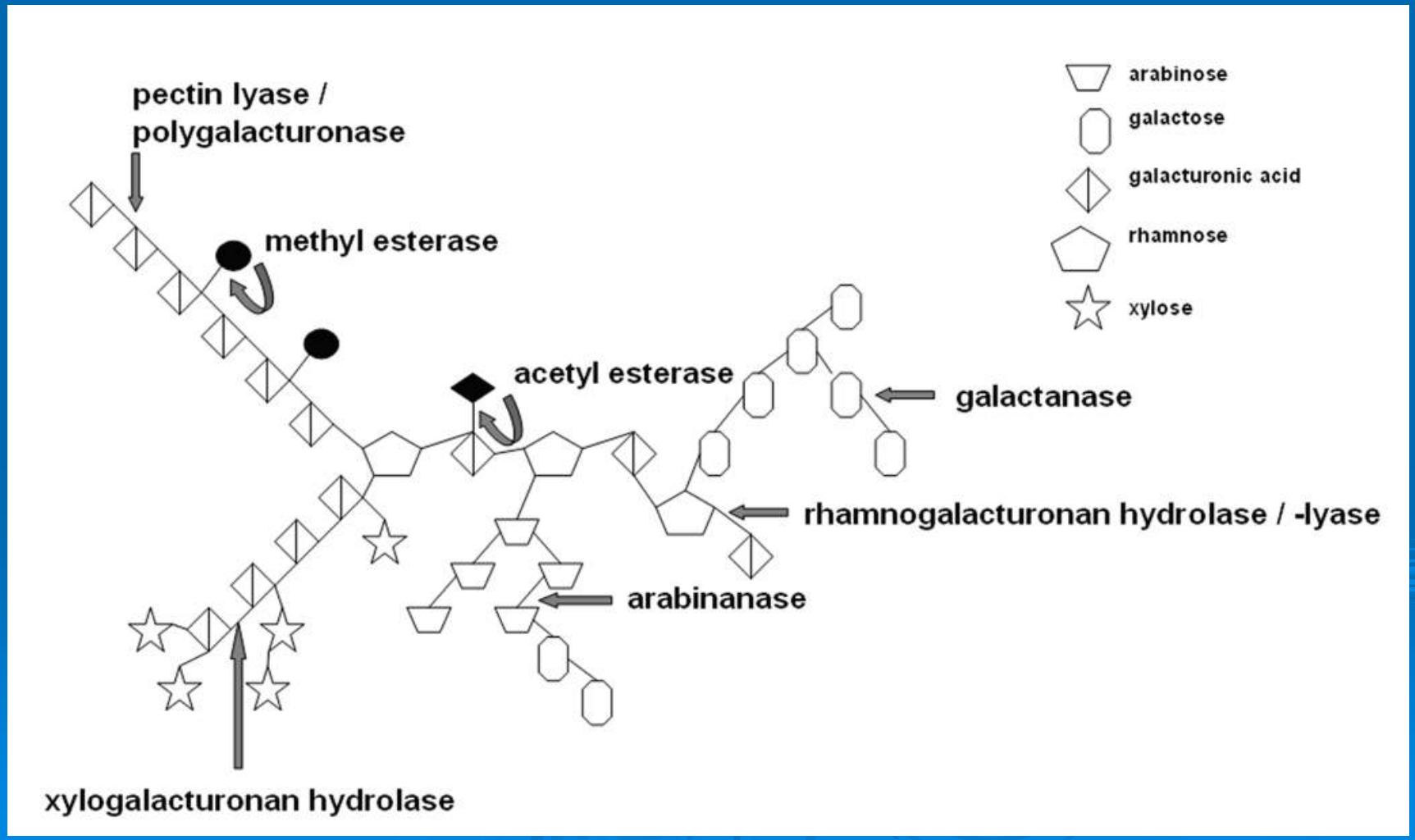
The structure of plant cell wall



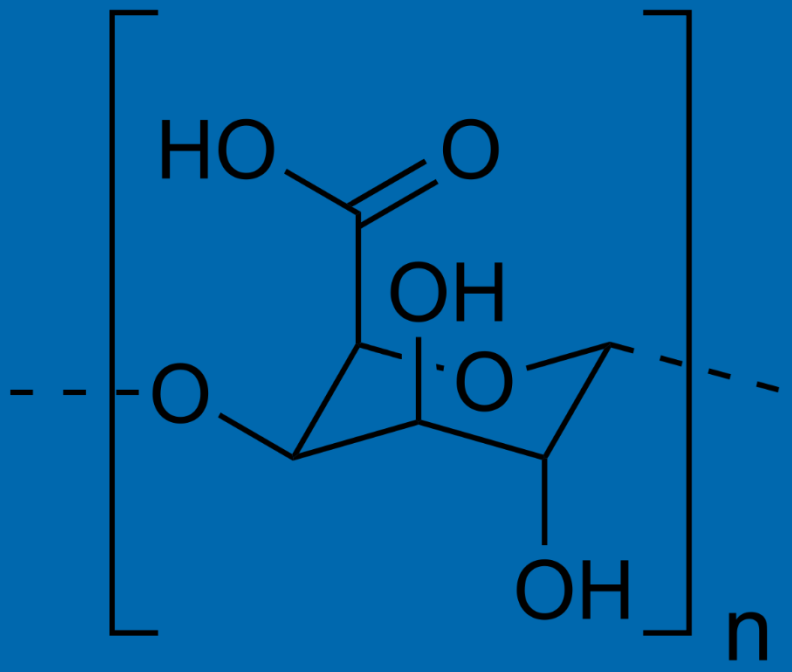
- Pectin is a family of galacturonic acid: rich polysaccharides including homogalacturonan, rhamnogalacturonan I, and the substituted galacturonans rhamnogalacturonan II (RG-II) and xylogalacturonan (XGA).
- Pectin biosynthesis is estimated to require at least 67 transferases including glycosyl-, methyl-, and acetyltransferases.

General structural organization of a pectin molecule

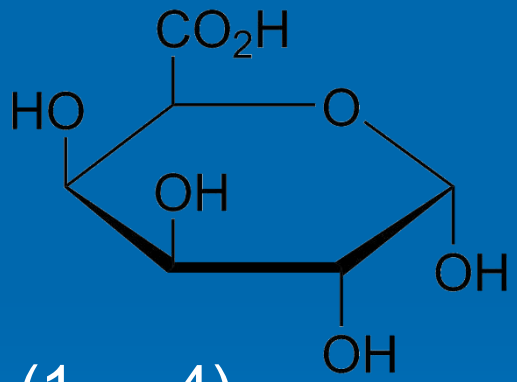
(H. Kokkonen, 2009)



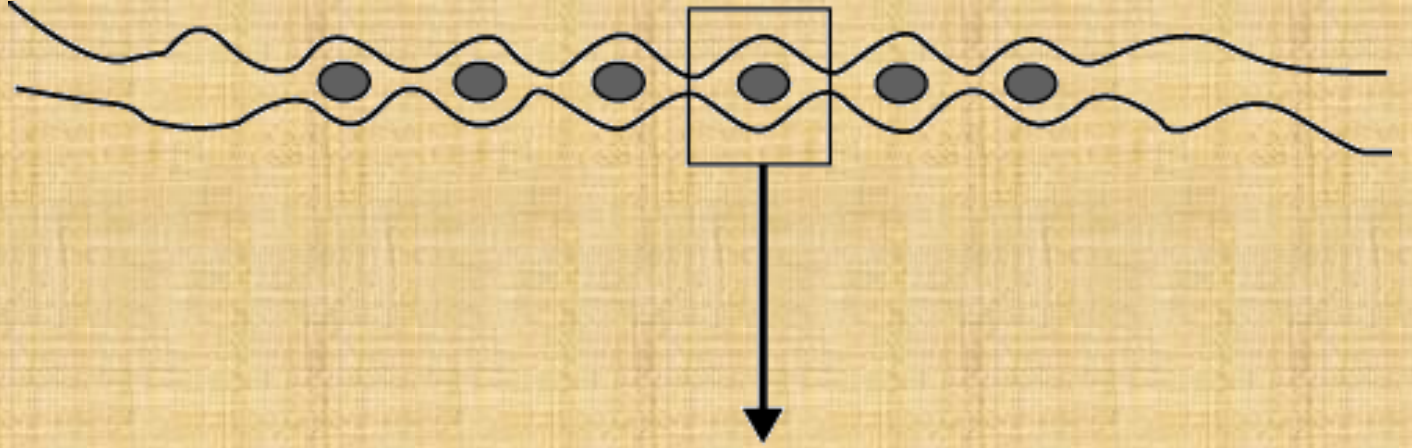
Pectic (polygalacturonic) acid

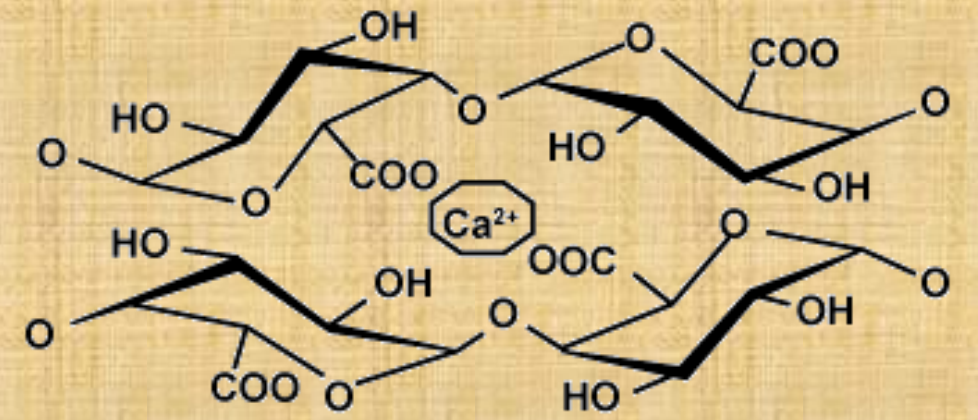


- Polyacid constructed from the residues of α-D-galacturonic acid bound with α-1,4 - glicoside bonds into long chains.



- Carboxylic groups of the residues of α-D (1 → 4)-galacturonic acids often exist as methyl esters (there are both low-methylated and high-methylated pectin with a degree of esterification of more than 50%)

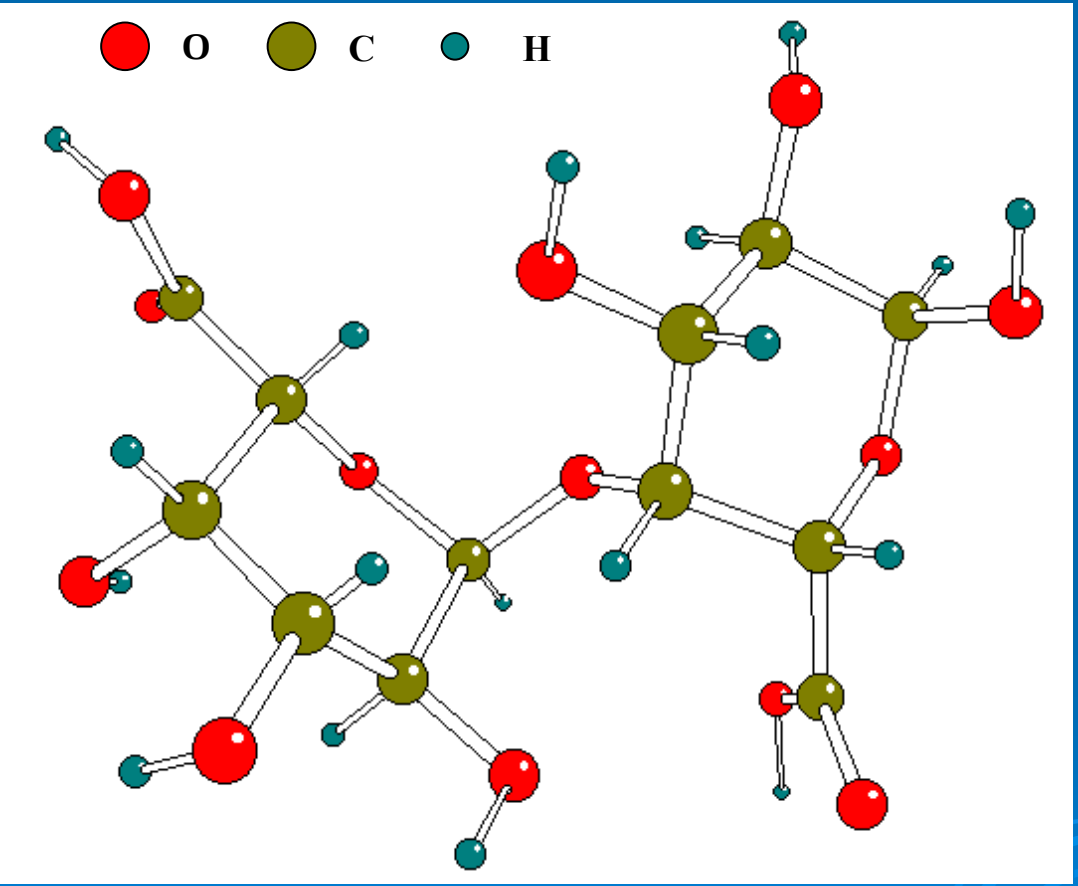



OH
HO
O
COO
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Ca2+
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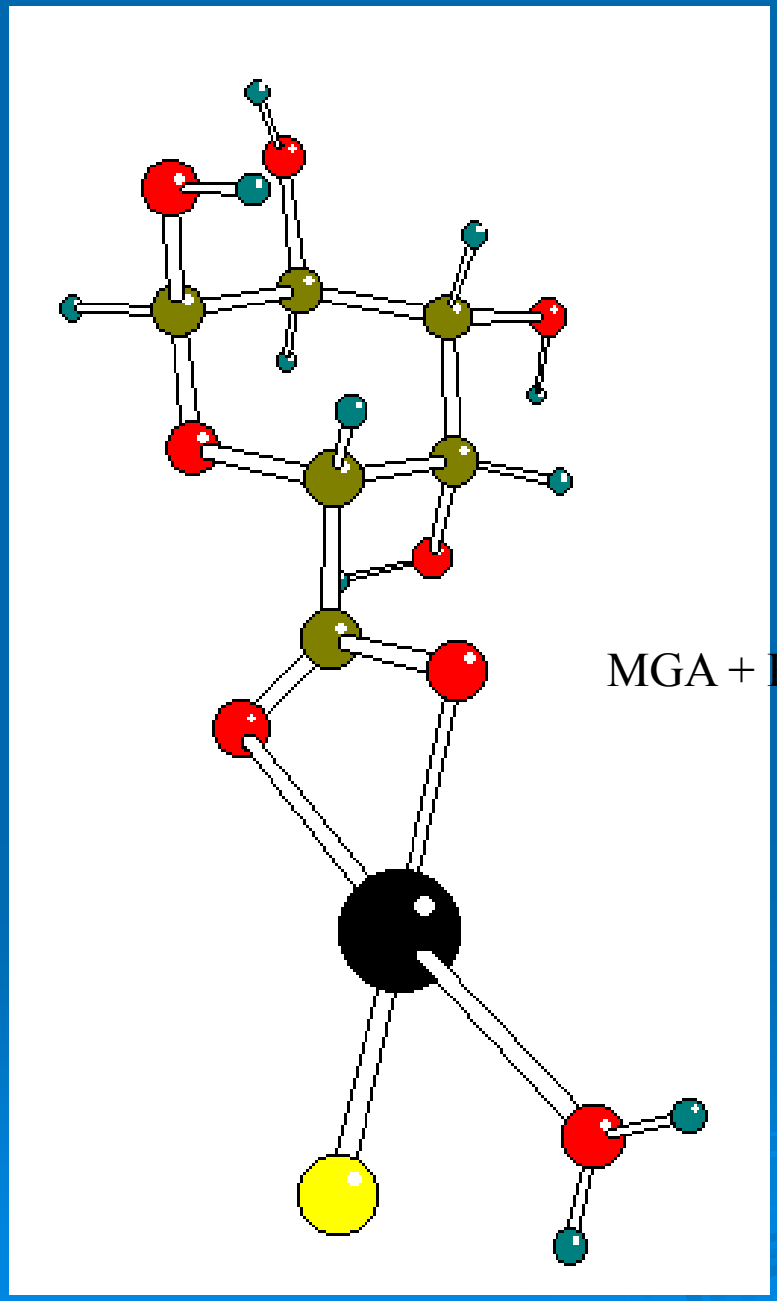
Examination on the equilibrium spatial structure of monomeric α-D-galacturonic acid (MGA), its dimer (DGA), trimer (TGA), tetramer (TeGA), pentamer (PGA), and hexamer (HGA) within the method of density functional theory (DFT) using the GAMESS program.

Performed together with colleagues from the Institute of Surface Chemistry

DGA molecule



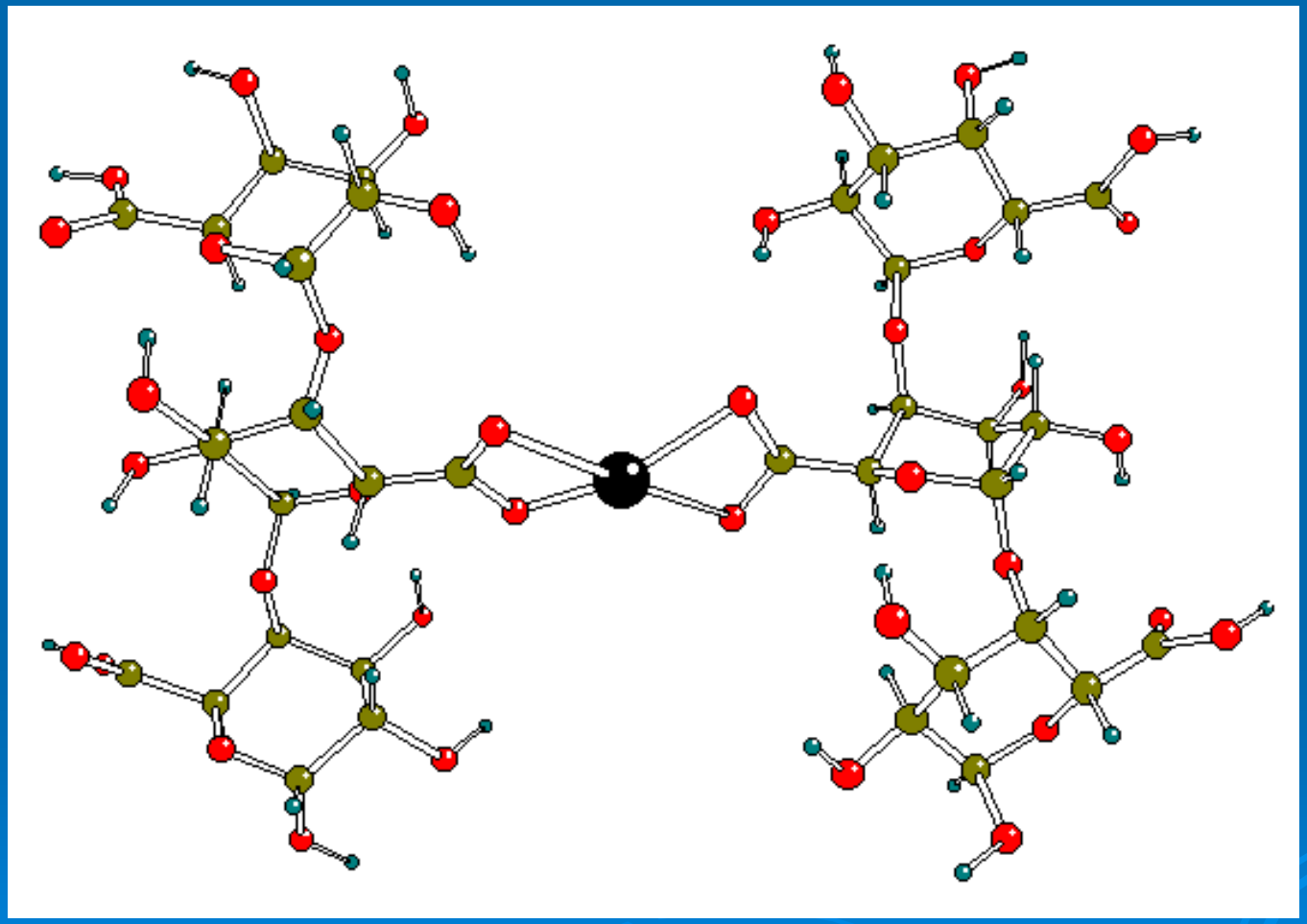
Equilibrium spatial structure of MGA and Hg ion



$$MGA + Hg[(H_2O{\bullet}Cl)_2] \rightarrow Hg\,[MGA{\bullet}Cl{\bullet}H_2O] + HCl + H_2O$$

O C H Hg Cl

Equilibrium spatial structure of $Hg[(TGK)_2]$



O C H Hg Cl

The acidity of polygalacturonic acids is naturally moderated with increase in the number of pyranose links in the main chain, reaching the minimum already at n = 6.

A partial methylation of the carboxyl groups of galacturonic acid residues, from one hand, moderates the amount of possible places of interlinking, and from other hand - results in an increase of acidity of unesterified part of carboxyl groups. It in turn contributes in an increase in durability of interlinking of hydrated metal ions.

Only carboxyl groups of galacturonic acid residues take part of a complex formation with hydrated mercury ions. An additional coordination of the central ion with formation of chemical bonds with carboxyl or hydroxyl groups of adjacent pyranose rings is impossible because of steric difficulties

Typical levels of pectin in fresh plants

- apples 1–1.5%
- sugar beet 1–2%
- apricots 1%
- cherries 0.4%
- oranges 0.5–3.5%
- carrots 1.4%
- pumpkin 1–1.4%
- citrus peels up to 30%

Isolated pectin has a molecular weight of typically 60,000–130,000 g/mol, varying with origin and extraction conditions

Pectin production

Pectin is extracted by adding hot dilute acid at pH-values 1.5–3.5. During several hours of extraction, the protopectin loses some of its branching and chain length and goes into solution. After filtering, the extract is concentrated in a vacuum and the pectin is then precipitated by adding ethanol or isopropanol.

Alcohol-precipitated pectin is then separated, washed and dried. Treating the initial pectin with dilute acid leads to low-esterified pectins. When this process includes ammonium hydroxide, amidated pectins are obtained.

УКРАЇНА

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B01J 20/30 (2006.01)

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(57) Реферат:

Спосіб отримання сорбенту з бурякового жому, що включає фізико-хімічну обробку сировини, висушування, причому буряковий жом обробляють спочатку розчином кислоти при pH 1,5…2,2 за температури 75…85 °С протягом 60…80 хвилин, потім розчином лугу при pH 10,0…11,0 протягом 15…20 хвилин, потім повторно обробляють розчином кислоти при pH 1,4…1,8 протягом 5…10 хвилин, нейтралізують розчином лугу та промивають водою до pH 6,5…7,5.

UA 124834 U

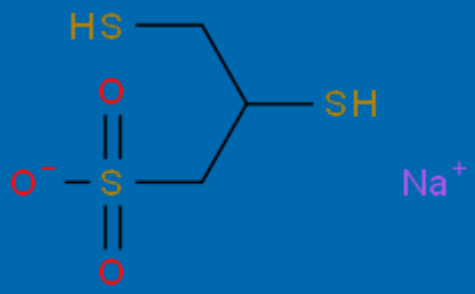
Patented pectin production

Pectin is extracted by adding acid at pH-values 1.5 – 2.2 for 60-80 min.; then followed by saponification by alkali at pH-values 10 – 11 for de-esterification purposes.

Afterwards acid is added again at pH-values 1.4 – 1.8 to form gel structures, then neutralized by adding alkali to reach pH-values 6.5 – 7.5. Pectin is then washed and dried.

Pectin vs. Unithiol

Dimercaptopropane sulphonate

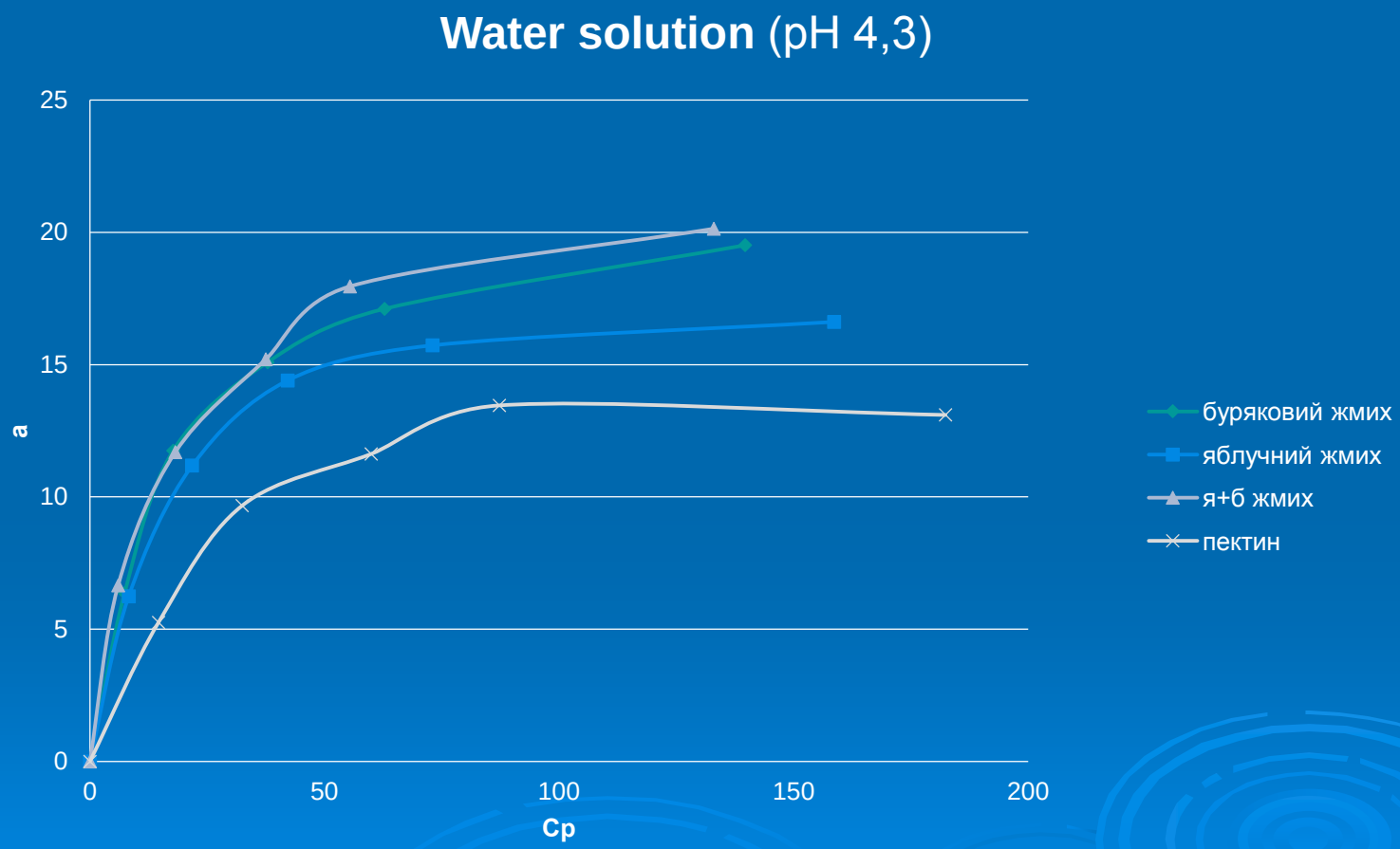




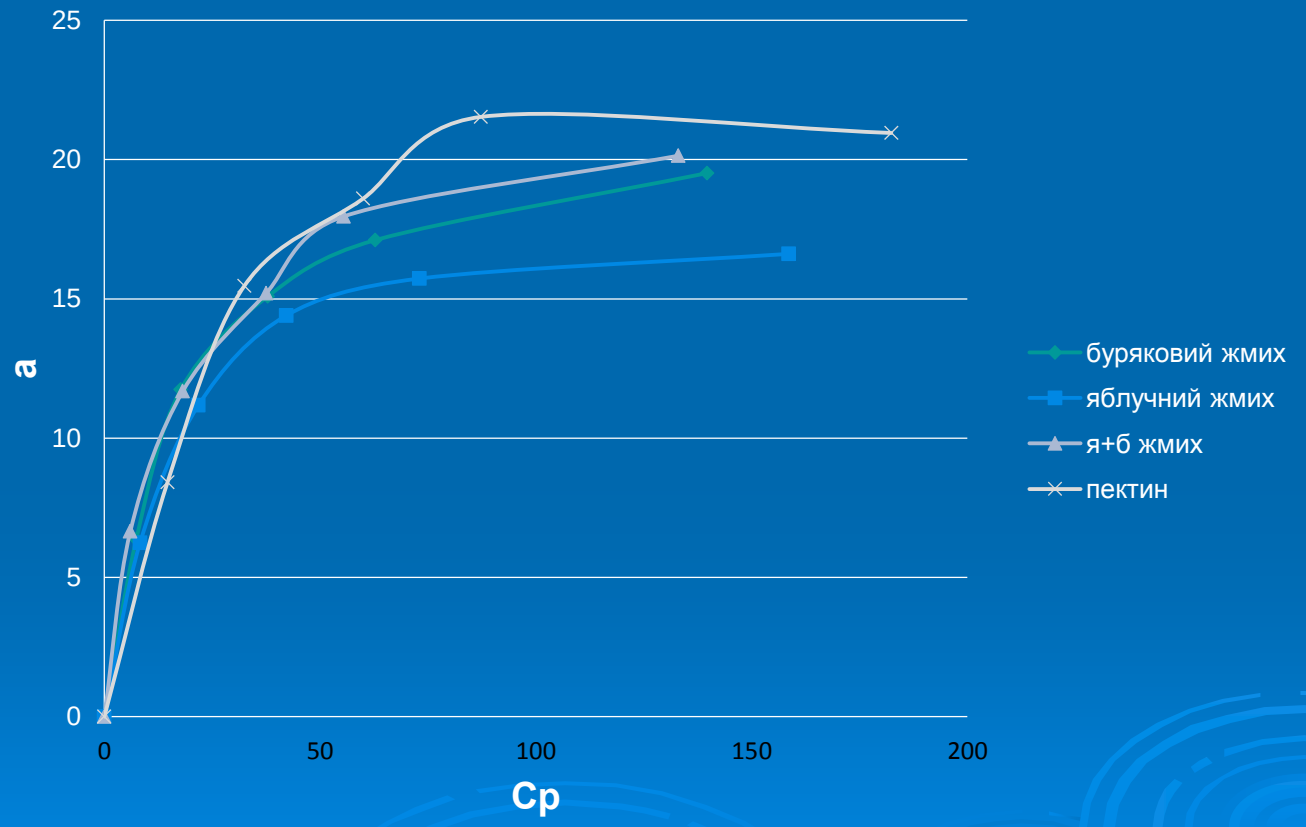




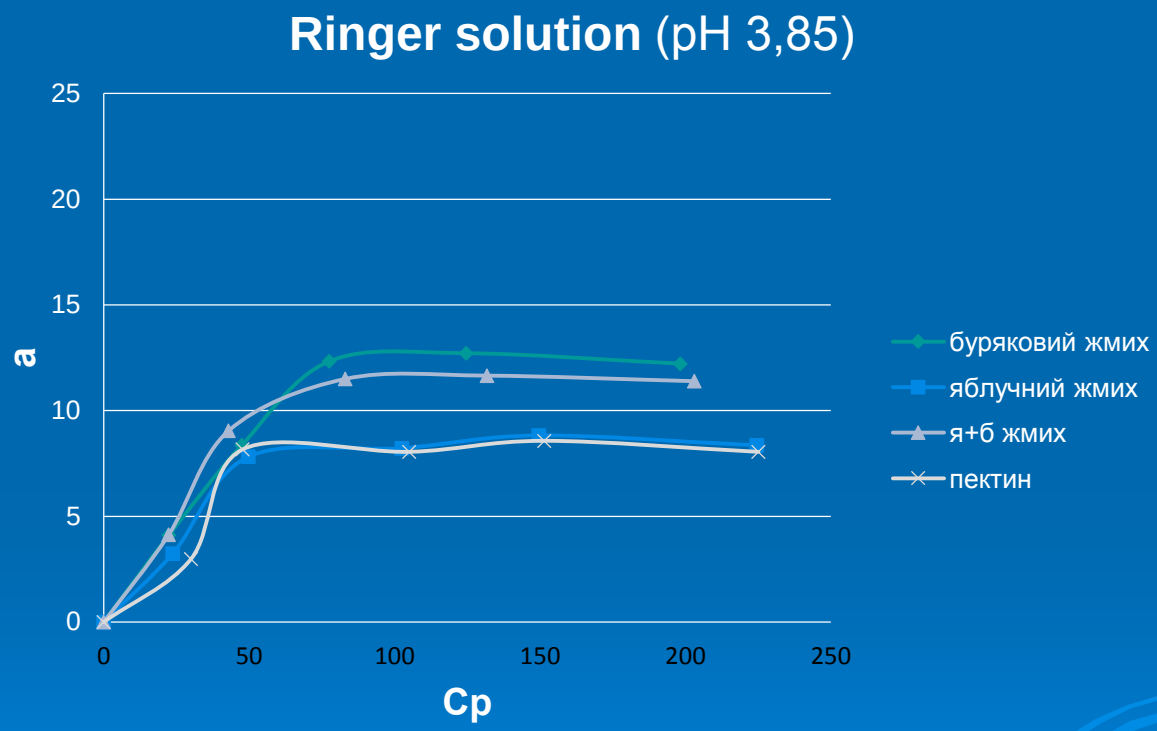
Sorption capacity of pectin comparing to raw materials ($PbAc_2$ in different concentrations)



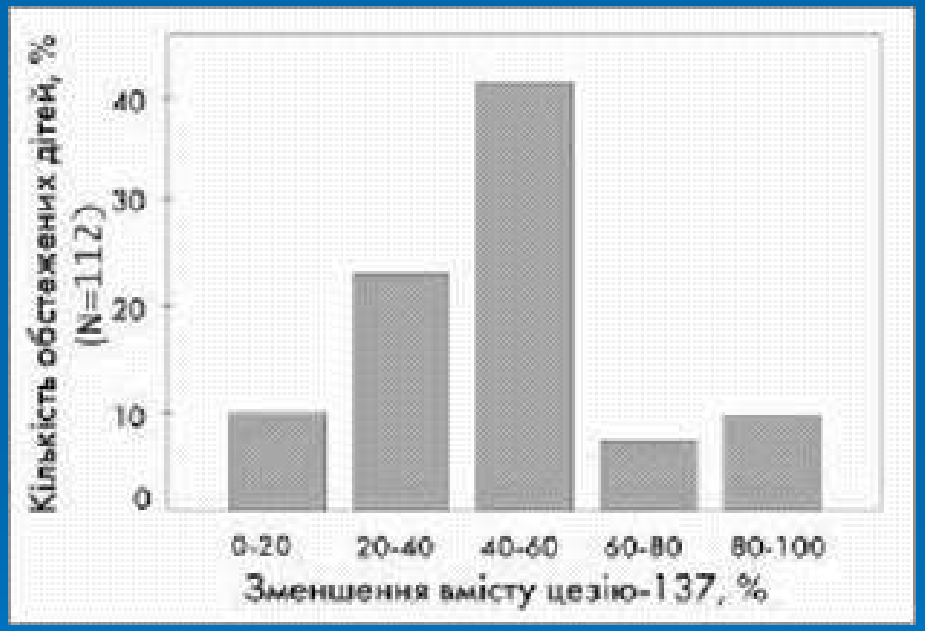
Sorption capacity of pectin comparing to raw materials (adjusted to 100% pectin)



Sorption capacity of pectin comparing to raw materials ($PbAc_2$ in different concentrations)



Pectin in reducing Cs-137 content

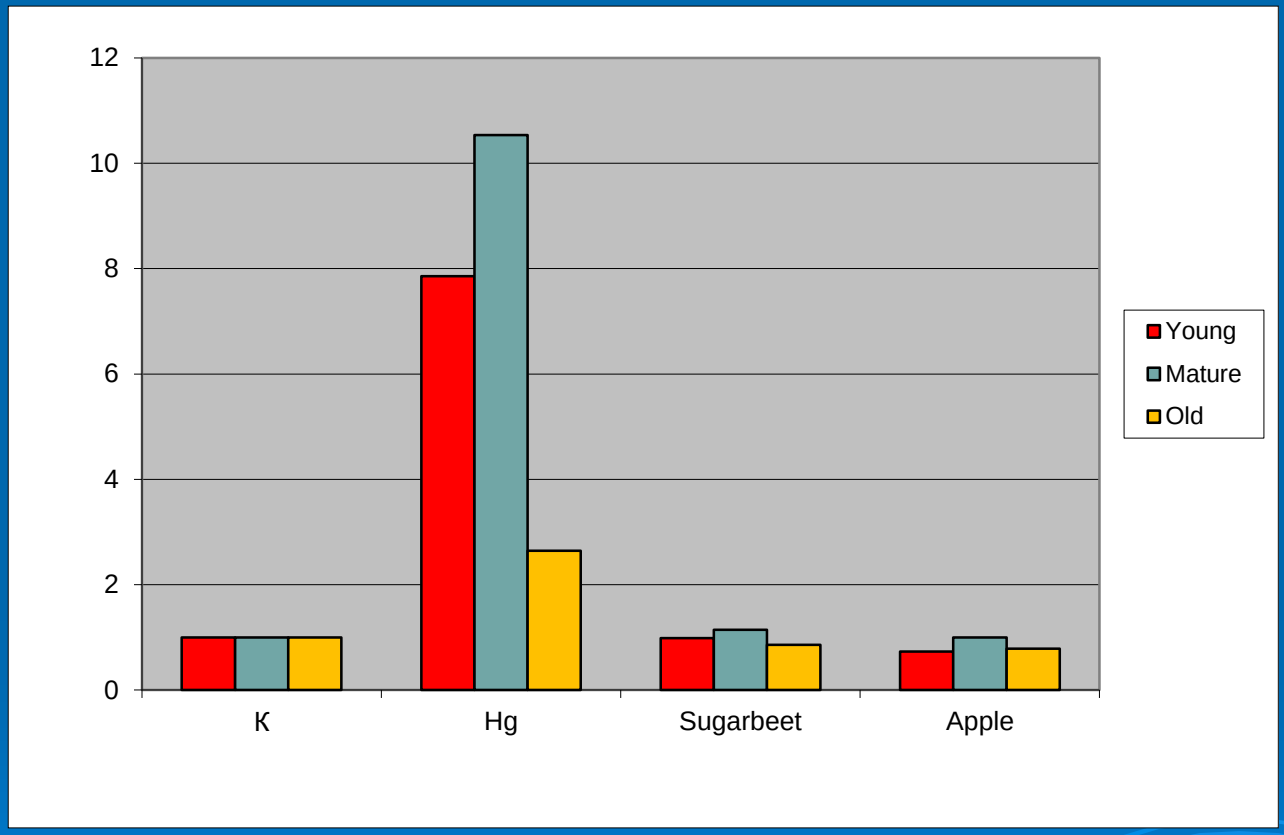


Former mercury mine
Fluorescent bulb recycling facility, Mykytivka

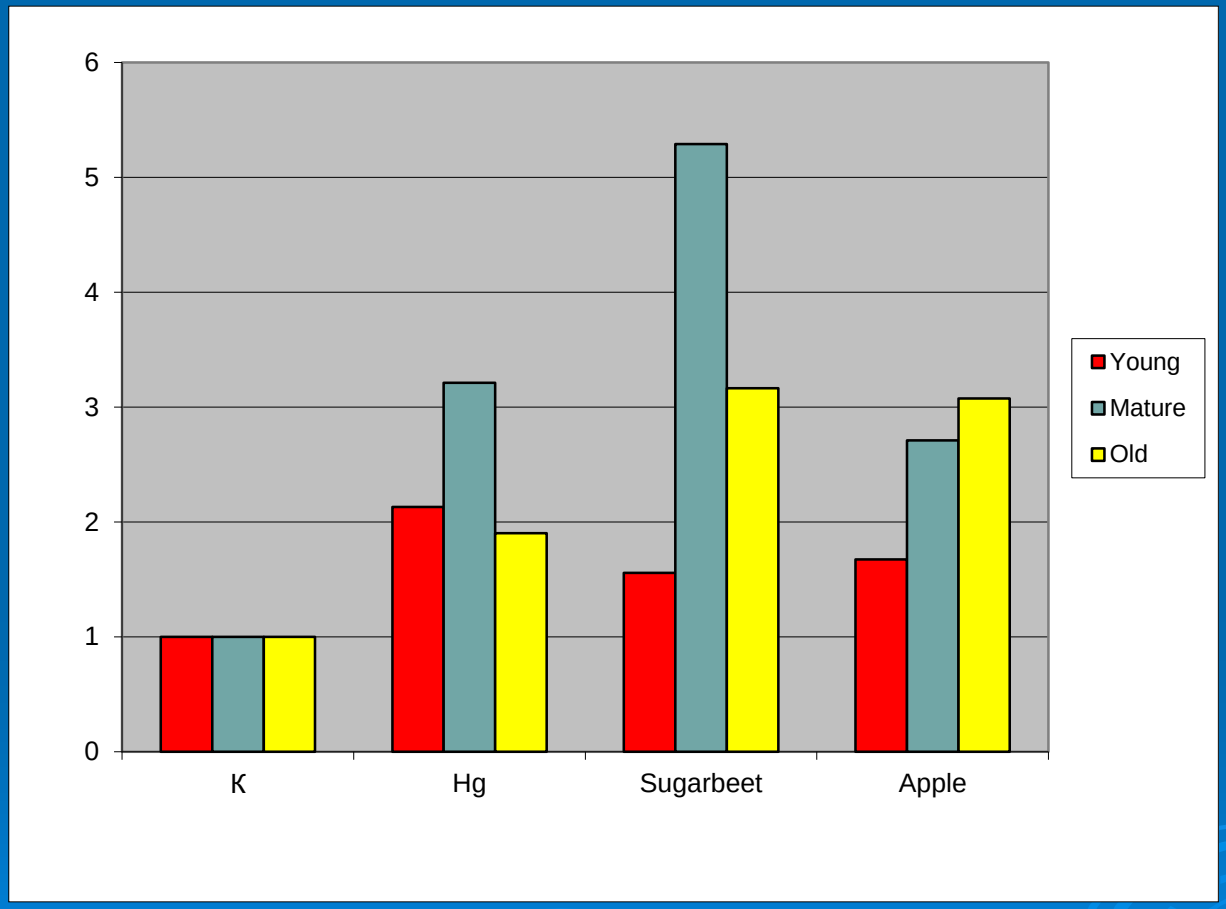




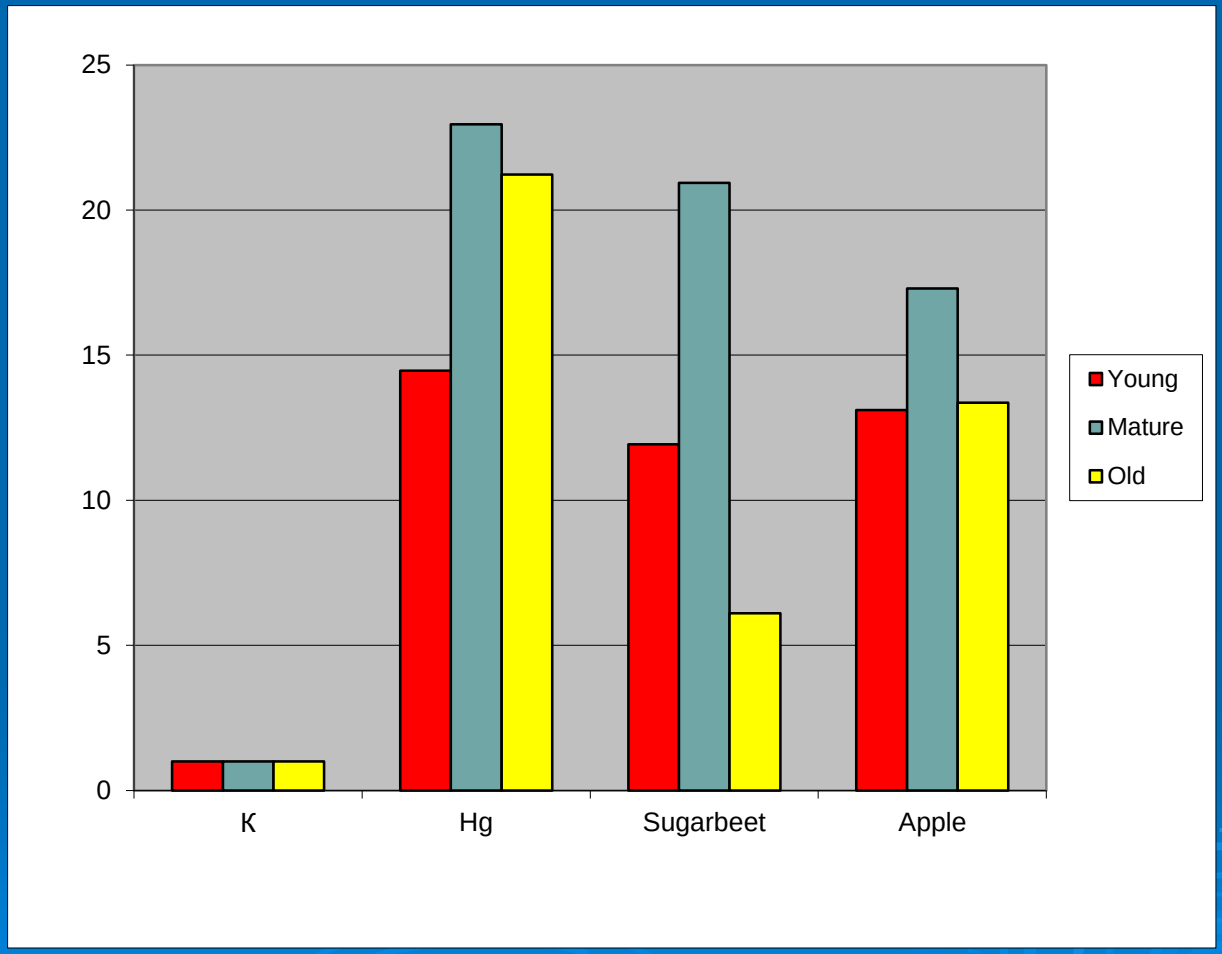
Mercury content in blood of rats of different age groups before and after pectin treatment



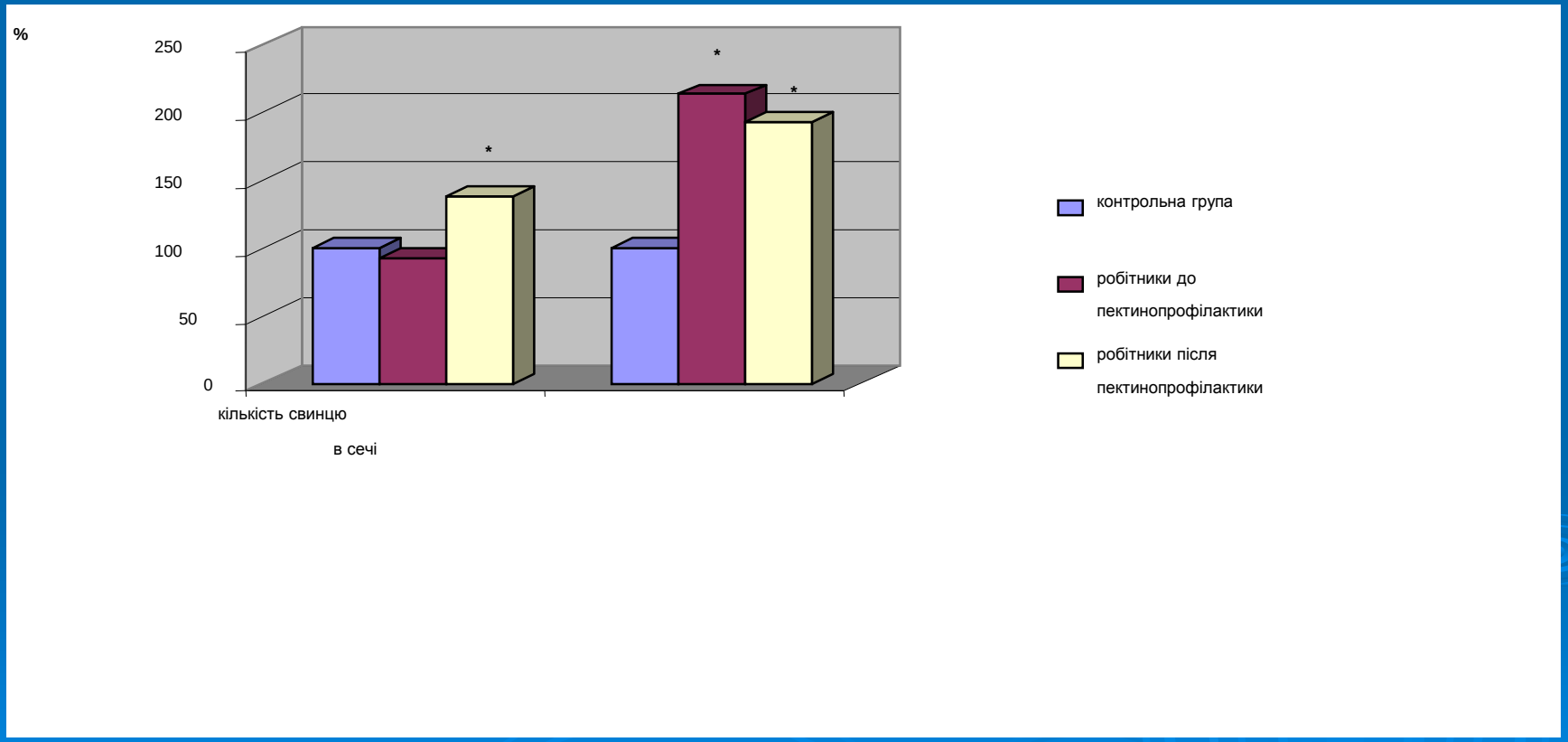
Mercury content in liver of rats of different age groups before and after pectin treatment



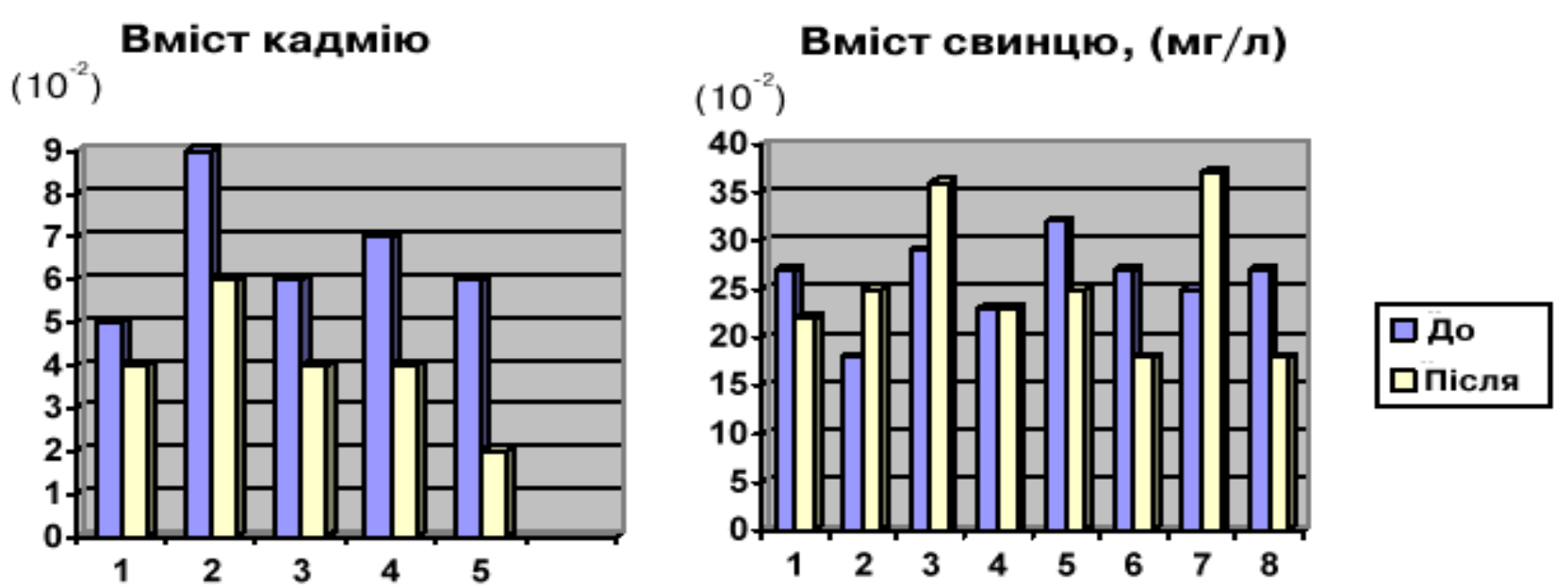
Mercury content in kidney of rats of different age groups before and after pectin treatment



Lead content in urine and blood of workers exposed to lead before and after administration of pectin
(in % to control group)



Application of pectin to reduce cadmium and lead content (mg/l) in blood of pregnant

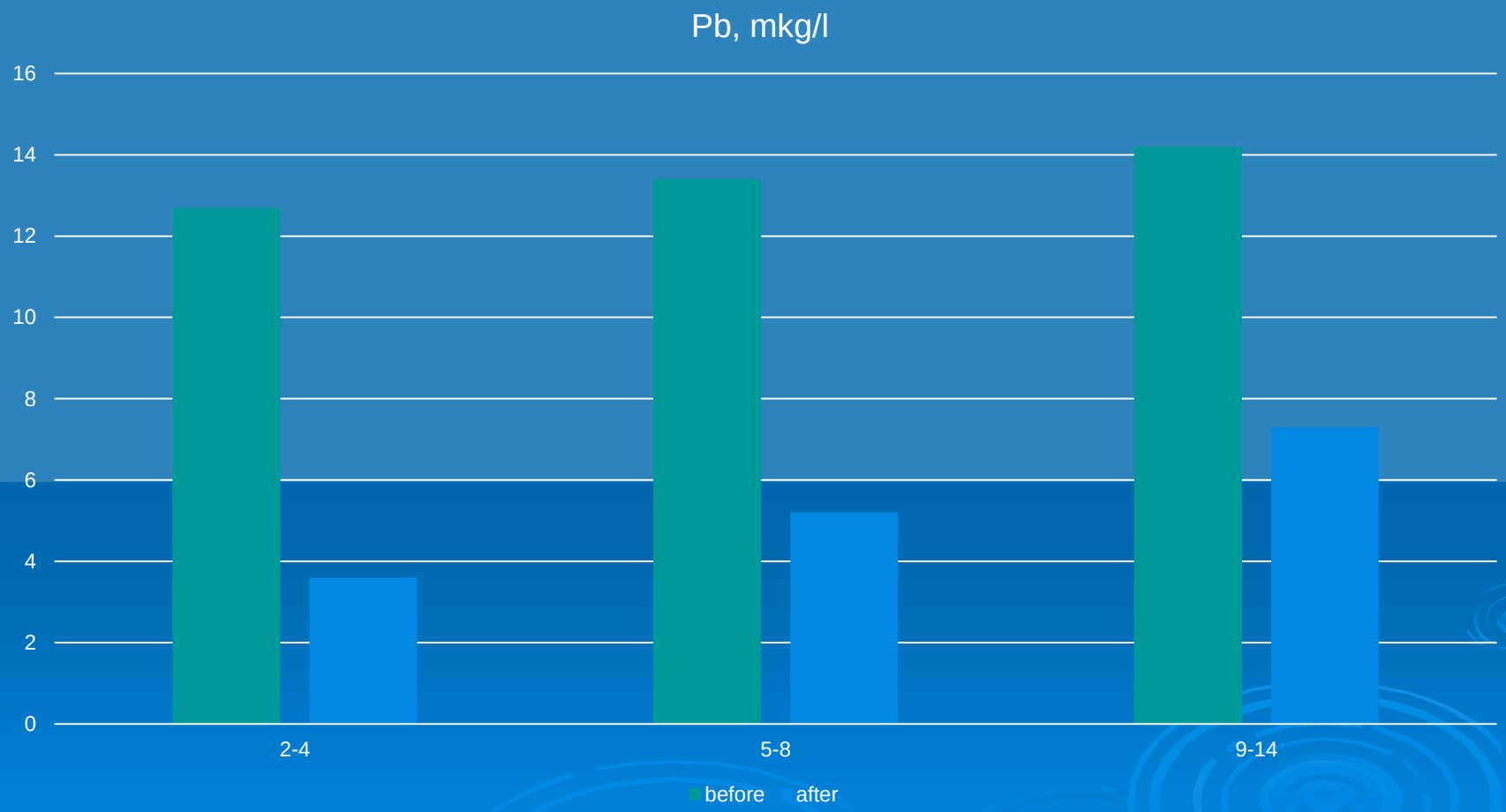


Vietnam project

- Đồng Mai village in Van Lam commune – artisanal processing of lead–acid batteries since ca. 1980 (June – September 2016)
- Bac Giang province (May – October 2017)

- Pectin Complex
- Pectin Technology Co. Ltd.
- Economic efficiency – 240 mln. VND (about 10,000 USD) per child

Children of Bac Giang province



Đồng Mai village

- 333 children and 107 adults (workers)

- 250 children examined before, 178 after:
- Above 45 mkg/l – 2/0;
- 11-44 mkg/l – 214/142;
- Below 10 mkg/l – 34/24
- Average decrease is from 20.94 to 16.92 mkg/l (21.1%)

Đồng Mai village

- 78 workers examined before, 54 after:
- Above 100 mkg/l – 2/0;
- 70-99 mkg/l – 9/4;
- 40-69 mkg/l – 34/9;
- Below 39 mkg/l – 33/41
- Average decrease is from 43.79 to 31.83 mkg/l (27.3%)

Next potential projects

- Remediation of former site of Radical factory in Kyiv
- Artisanal gold mining in Peru

Summary

- Patented technology
- Production is carried out according to Ukrainian standards (TU U 15.8-16475490.001-2001)
- Several researches on efficiency in medical practice.
- At the moment about 650,000 therapeutic doses were produced.