NAZARBAYEV UNIVERSITY

Environmental Science & Technology Group

MACROPOROUS CRYOGEL COMPOSITES FOR REMOVAL OF HEAVY METALS FROM AQUEOUS AND BIOLOGICAL MEDIA

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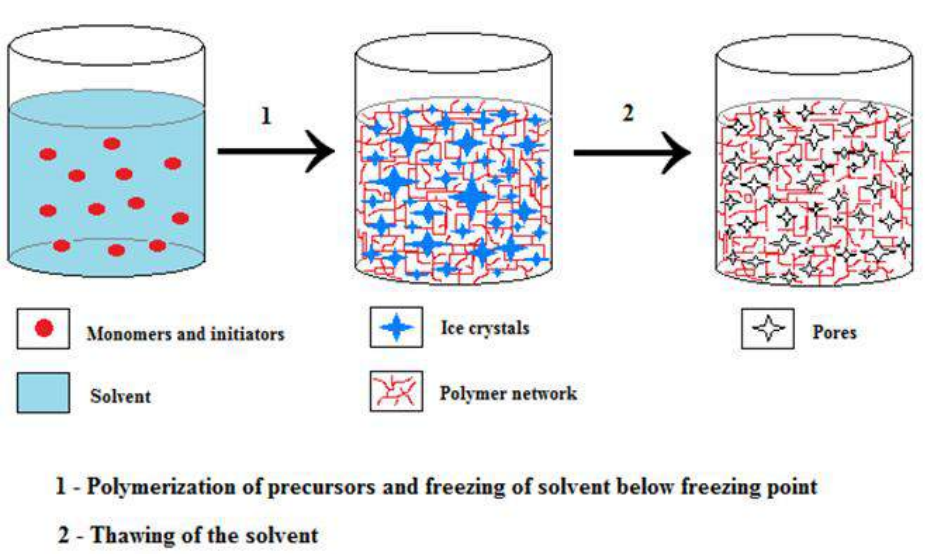
Dr. Dmitriy Berillo (*external*, Aarhus University, Denmark)

Budapest, 2018

Cryogel: a novel multifunctional material

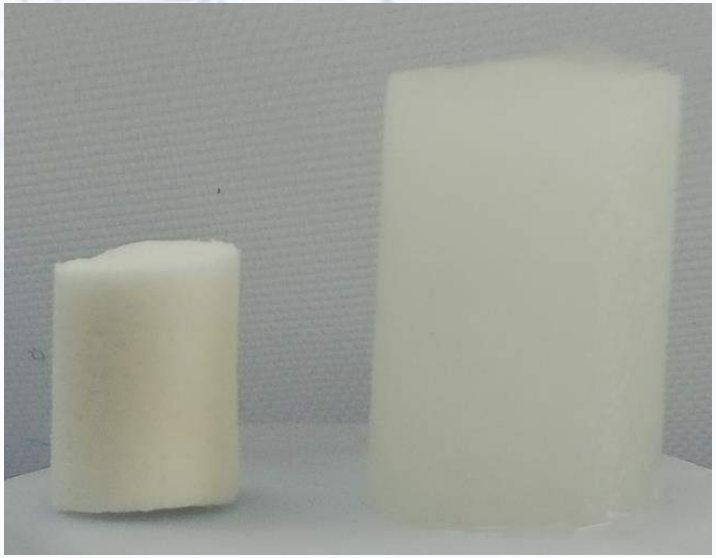
What is cryogel?

- Cryogel is a macroporous hydrogel produced by freezing-thawing method
- Depending of monomer selection different functional groups can be obtained



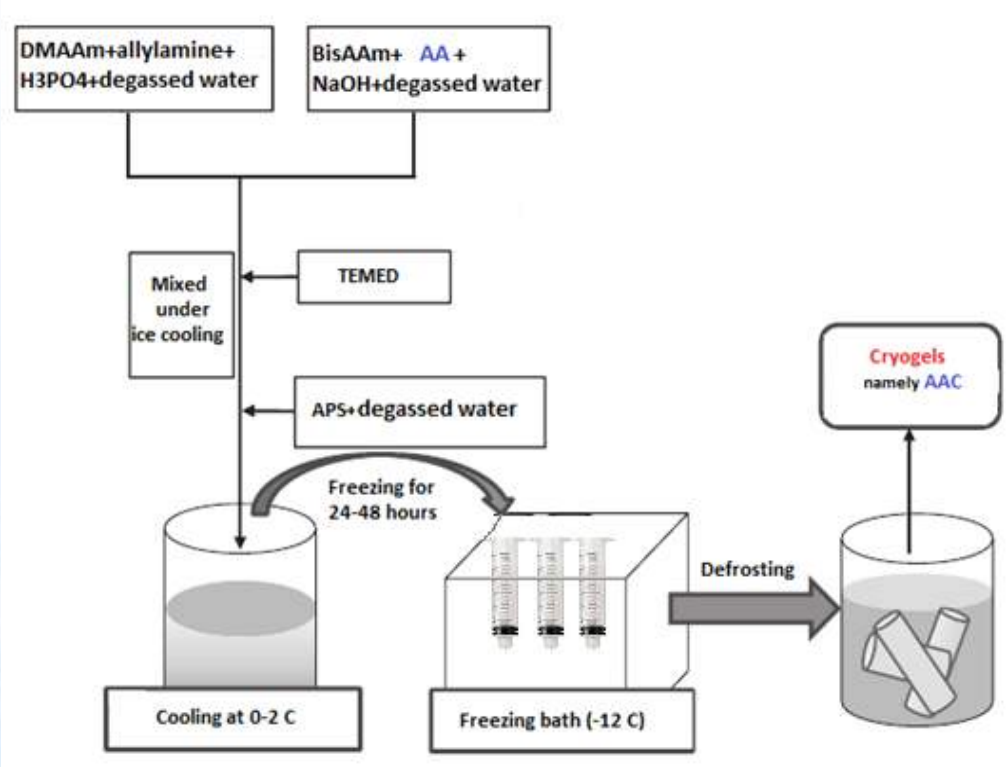
Advantages of Cryogels:

- Larger surface area
- Higher cation/anion exchange capacity
- Modification capability
- Good elasticity



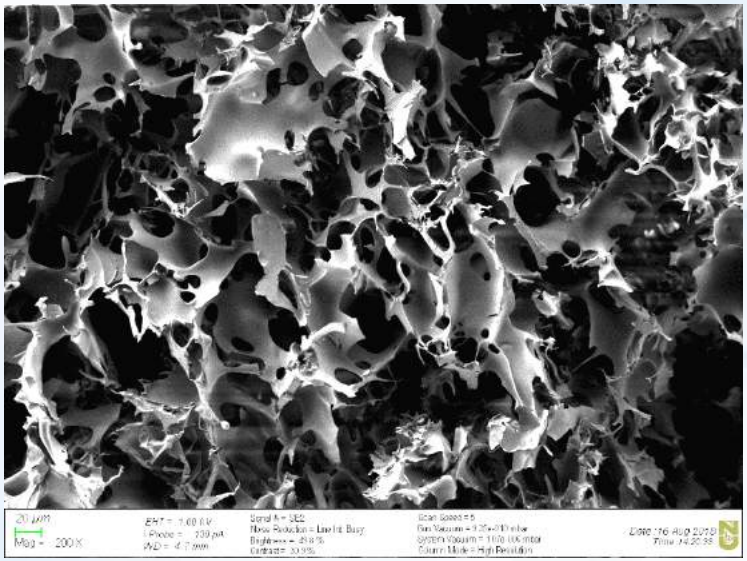
(left) Dry and (dry) water swollen cryogel

Schematic steps of cryogels synthesis

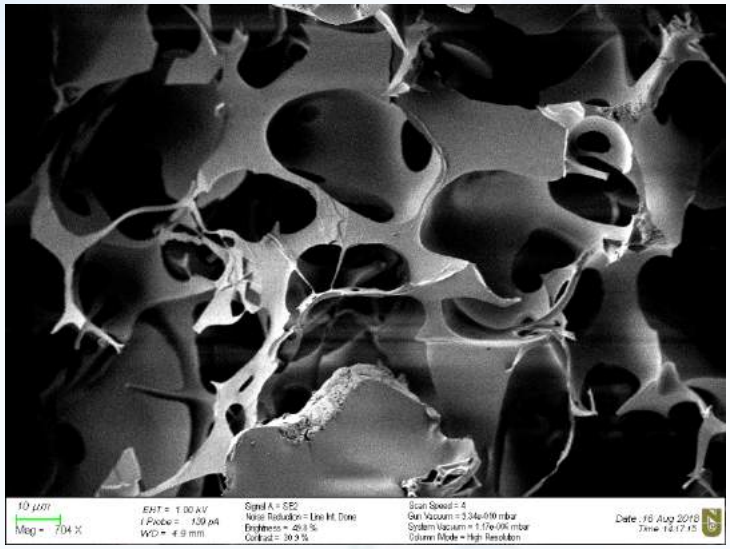


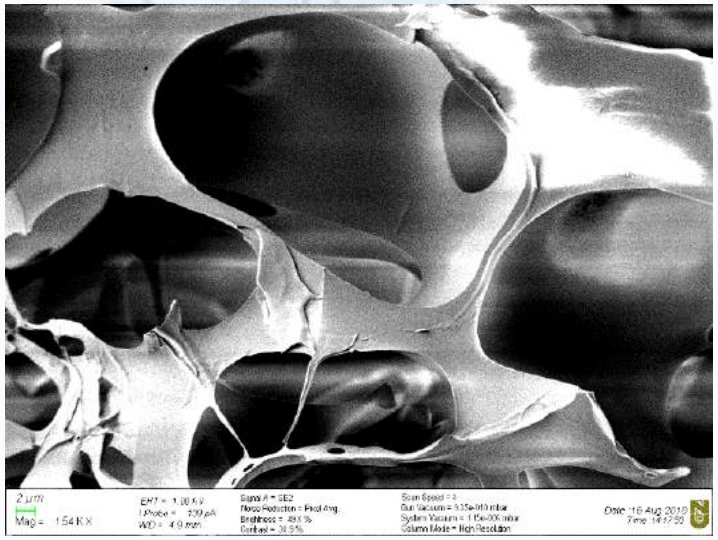
Material	Role
m-acrylic acid, allylamine, Dimethyl acrylamide	Monomers
Bisacrylamide	Cross-linker
Ultra pure water	Solvent
Ammonium persulfate (APS)	Oxidant
Tetramethyl ethylenediamine ()	Reductant
Phosphoric acid, sodium hydroxide	Functional groups formers

SEM images of AAC cryogel



Element	Wt%	At%
CK	64.47	70.57
NK	12.44	11.68
OK	18.21	14.97
NaK	4.88	2.79
Matrix	Correction	ZAF

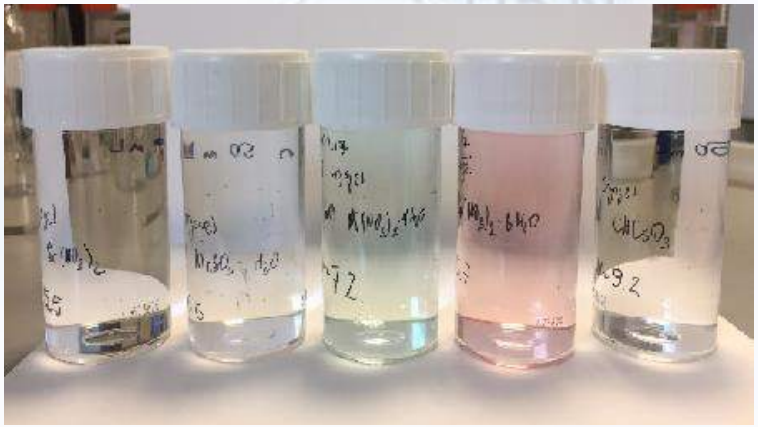




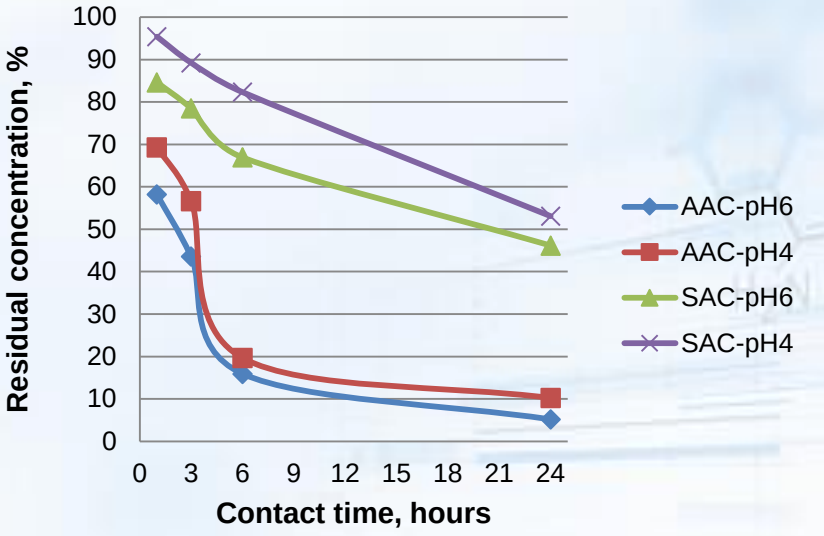
Heavy metal removal using synthesized cryogels

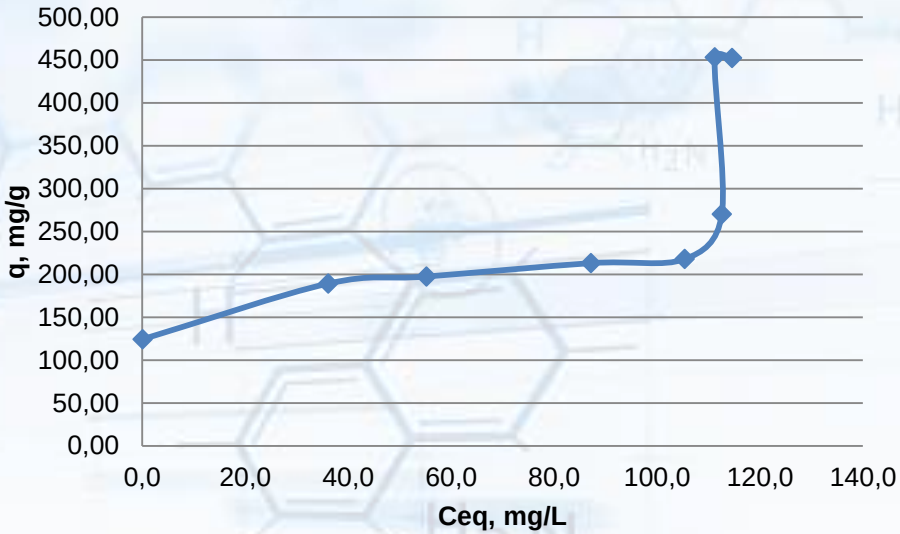
- Removal of targeted metals (Cd(II), Sr(II), Cs(I), Hg(II)) were made in static mode by adding one monolithic cryogel (weight 80 mg) to 100 ml 100 ppm solution of selected metal.
- Cryogels were incubated in metal solutions for 24 h at RT.
- All of the solutions were filtered using 0.22 um membrane and diluted by 50-100 times in order to be analyzed by Inductively coupled plasma mass spectrometry (ICP-MS) or mercury analyzer depend on metal ions .





Results of Cd(II) removal

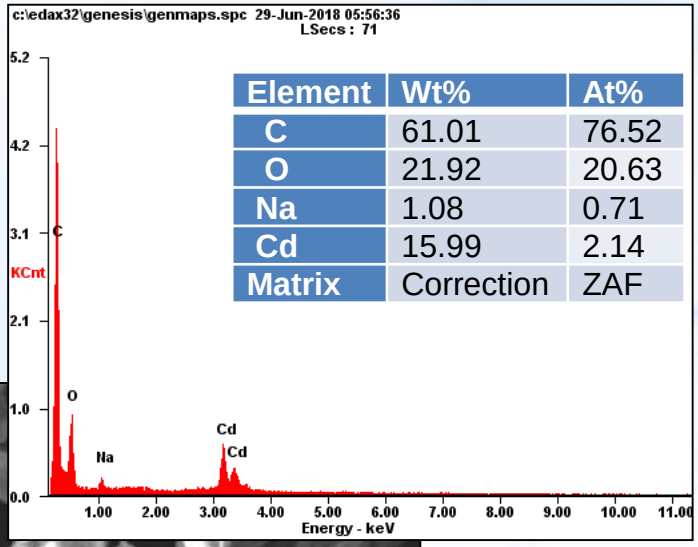




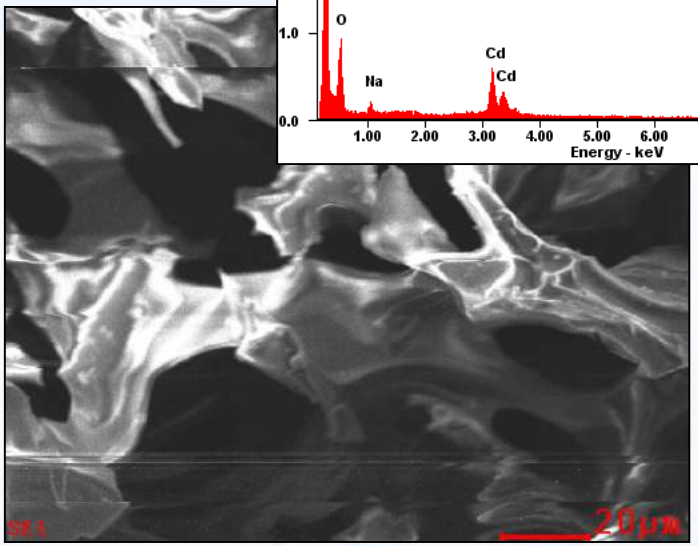
One g of AAC cryogel able to remove 123 mg/g at pH= 6.0 and 116 mg/g of Cd at pH=4,1 in 24 h.

Maximum capacity of 1 g AAC cryogel is 450 mg of Cd(II)

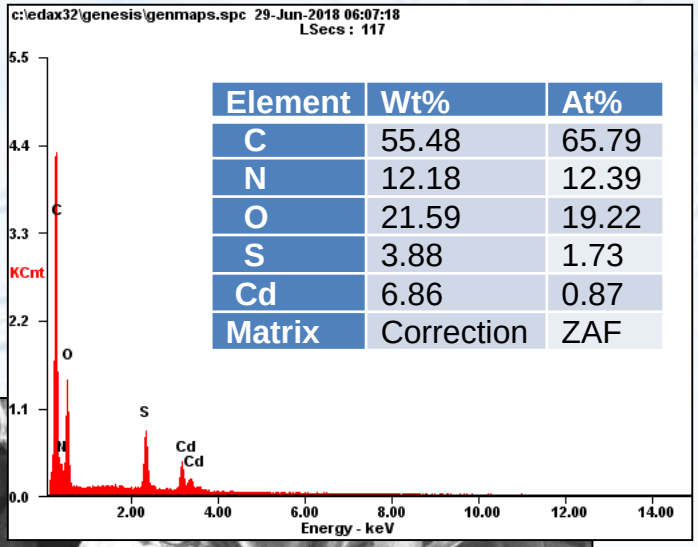
EDS results of cryogels after Cd(II) removal



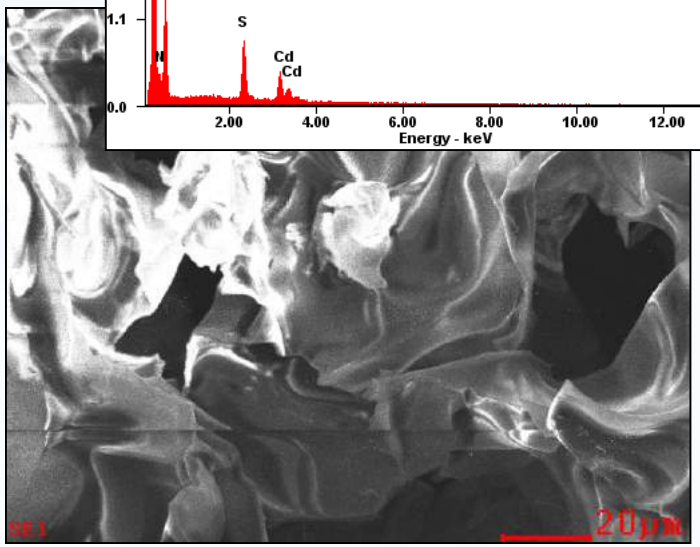
Element	Wt%	At%
C	61.01	76.52
O	21.92	20.63
Na	1.08	0.71
Cd	15.99	2.14
Matrix	Correction	ZAF



AAC cryogel

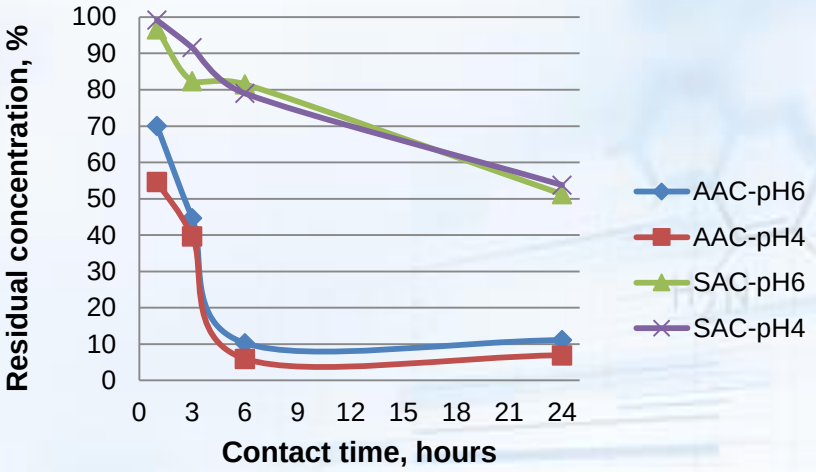


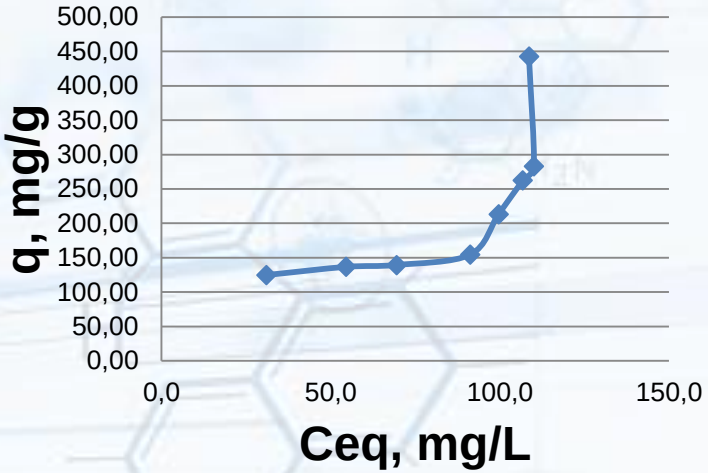
Element	Wt%	At%
C	55.48	65.79
N	12.18	12.39
O	21.59	19.22
S	3.88	1.73
Cd	6.86	0.87
Matrix	Correction	ZAF



SAC cryogel

Results of Sr (II) removal

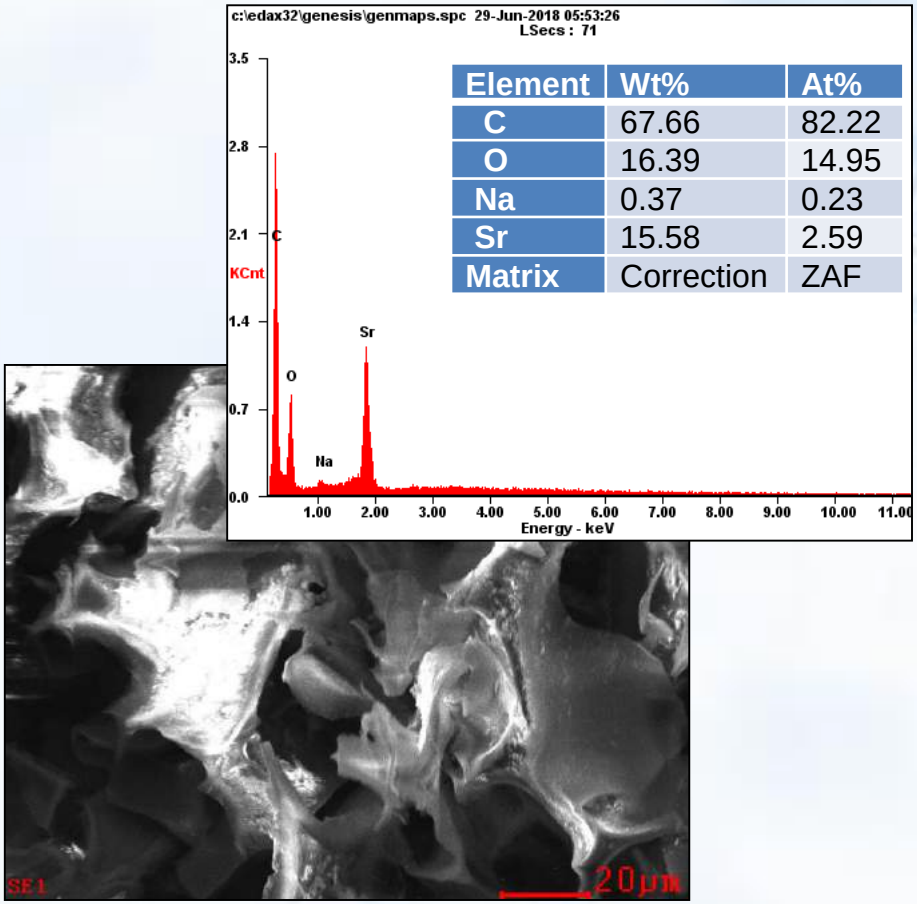




1 g of AAC cryogel able to remove 106 mg of Sr(II) at pH= 6.0 and 110mg of Sr at pH=4,0 in 24 hours.

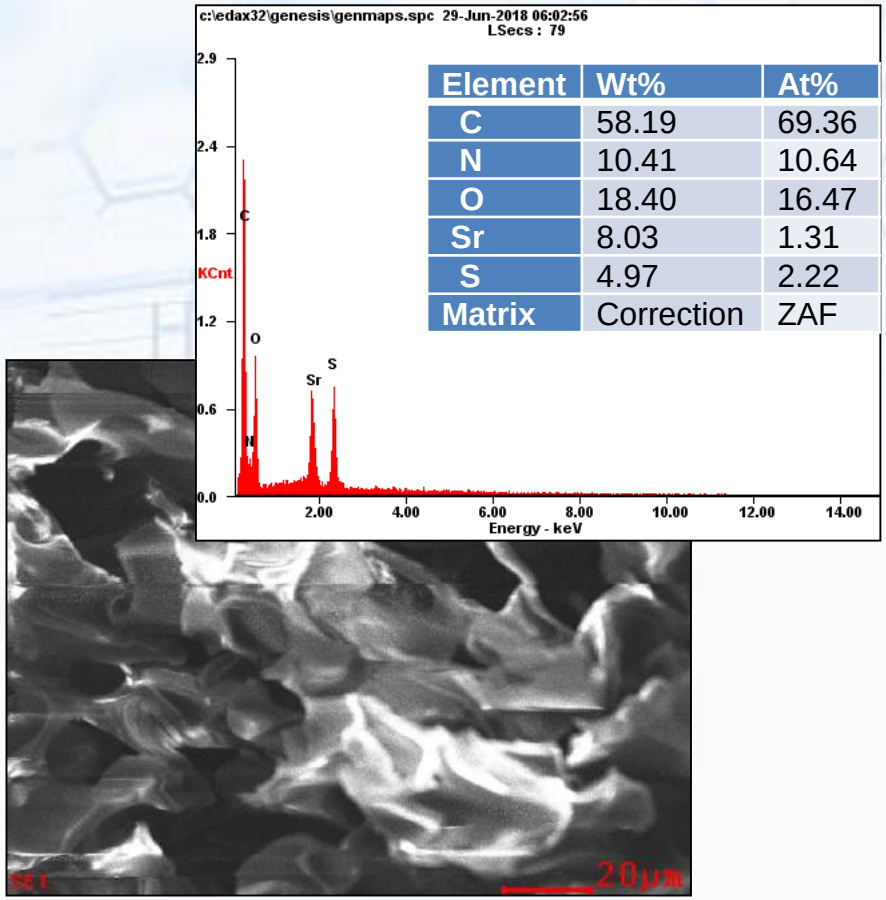
Maximum capacity of 1 g AAC cryogel is 450 mg of Sr(II)

EDS results of cryogels after Sr(II) removal



Element	Wt%	At%
C	67.66	82.22
O	16.39	14.95
Na	0.37	0.23
Sr	15.58	2.59
Matrix	Correction	ZAF

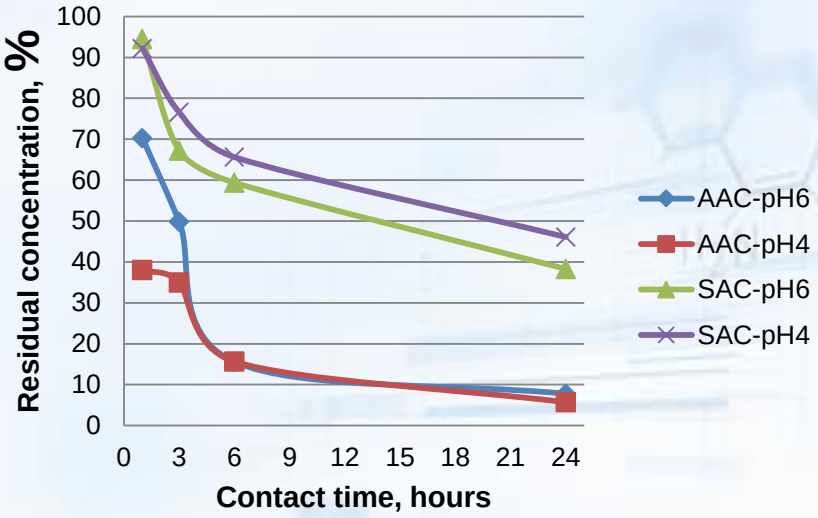
AAC cryogel

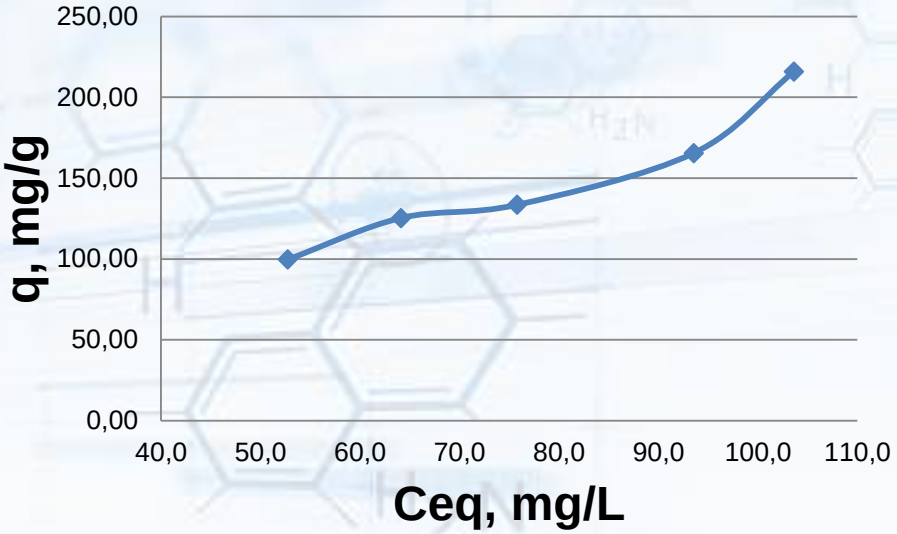


Element	Wt%	At%
C	58.19	69.36
N	10.41	10.64
O	18.40	16.47
Sr	8.03	1.31
S	4.97	2.22
Matrix	Correction	ZAF

SAC cryogel

Results of Cs (I) removal

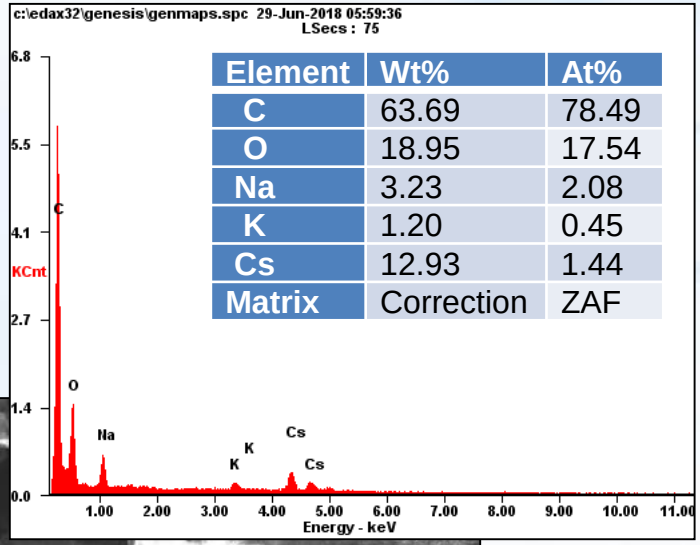




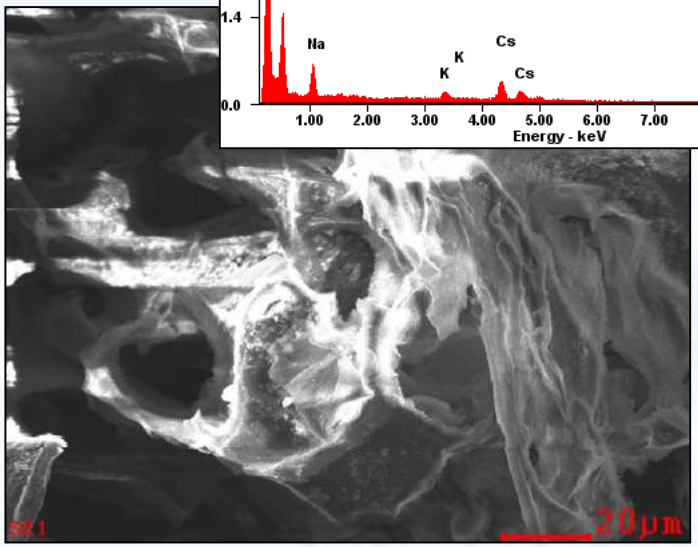
1 g of AAC cryogel able to remove 118 mg of Cs at pH= 6.0 and 120 mg of Cs at pH=4,0.

Maximum capacity of 1 g AAC cryogel is 220 mg of Cs(I)

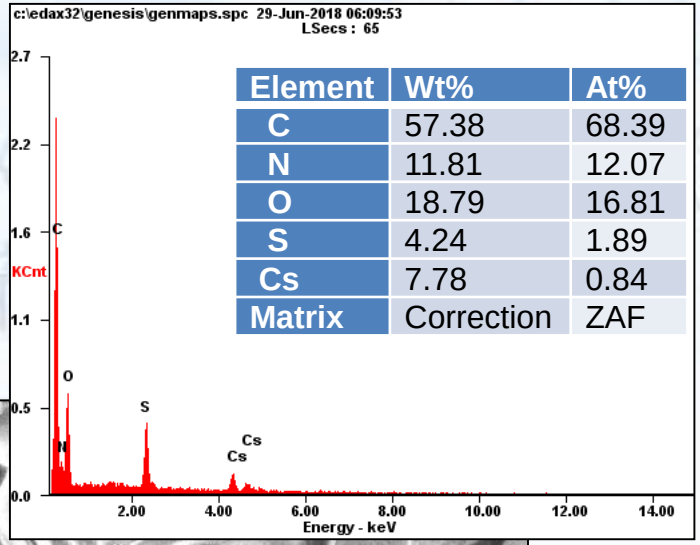
EDS results of cryogels after Cs(I) removal



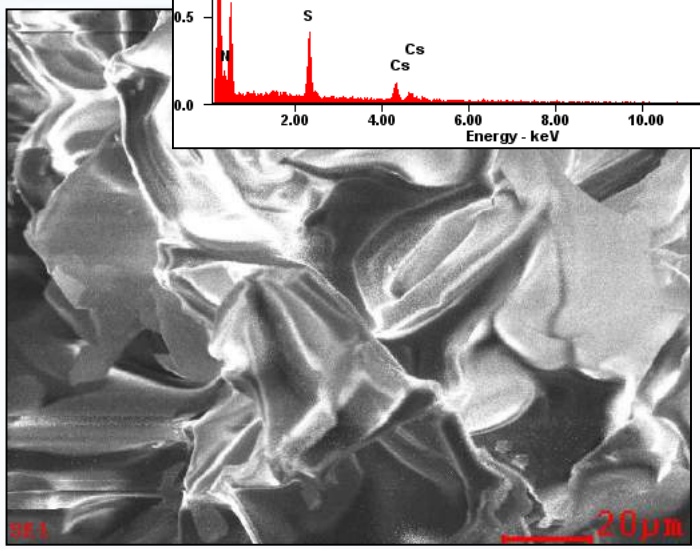
Element	Wt%	At%
C	63.69	78.49
O	18.95	17.54
Na	3.23	2.08
K	1.20	0.45
Cs	12.93	1.44
Matrix	Correction	ZAF



AAC cryogel

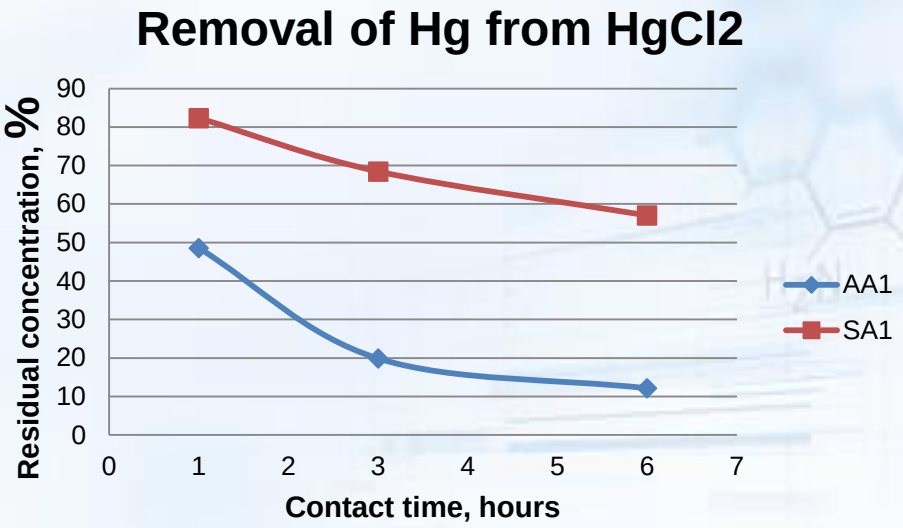


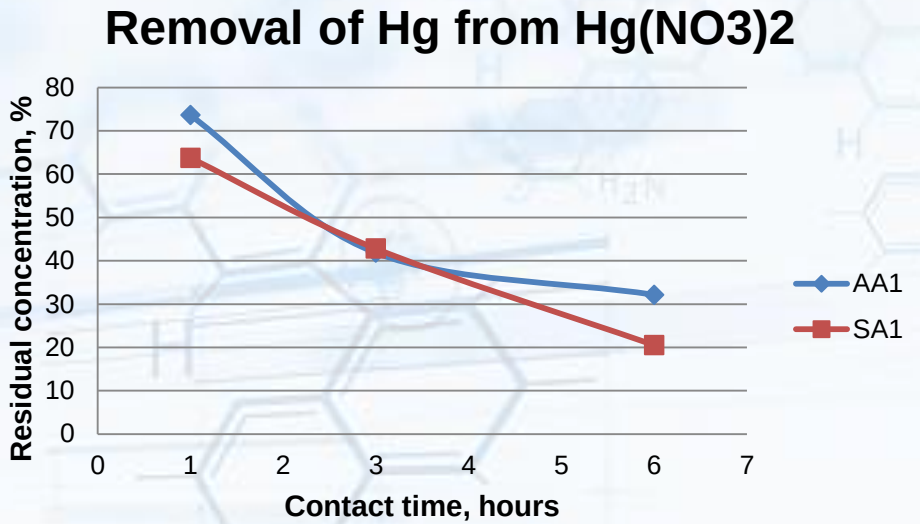
Element	Wt%	At%
C	57.38	68.39
N	11.81	12.07
O	18.79	16.81
S	4.24	1.89
Cs	7.78	0.84
Matrix	Correction	ZAF



SAC cryogel

Removal of Hg(II) by AAC and SAC cryogels





1 g of AAC cryogel able to remove 134 mg of Hg(II) from HgCl2 and 81 mg of Hg(II) from Hg(NO3)2

1 g of SAC cryogel able to remove 65 mg of Hg(II) from HgCl2 and 90 mg of Hg(II) from Hg(NO3)2

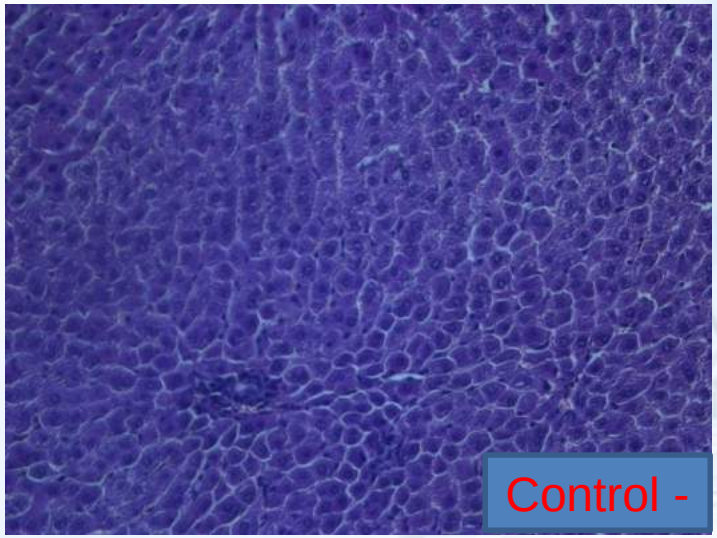
In vivo animal experiments

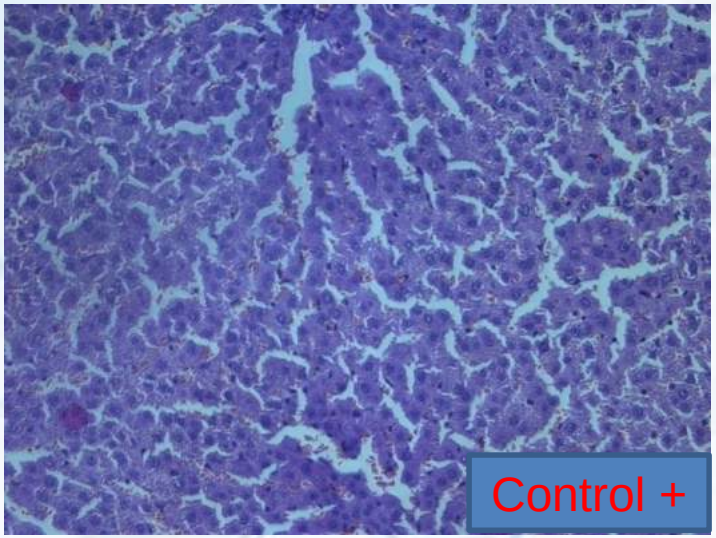
- In vivo animal experiments were conducted at Kazakh National Medical University (KazNMU), Almaty with approval of Local Ethical Committee of KazNMU.
- To model acute intoxication with Cd(II), Sr(II), Cs(I) and Hg(II) (all metals were used separately) oral route has been selected. Male mongrel rats, weighing 180-220 g, in groups of 10 heads for each dose of metal and for the positive and negative control groups were used.
- Introduction of cryogels was done by oral route, through an atraumatic probe in the form of a suspension at doses of 250 mg/kg in a 15 ml saline solution. As a comparison was used commercial chelating agent – unithiol (was bought in a pharmacy) with the dose 250 mg/kg (3 rats per metal).

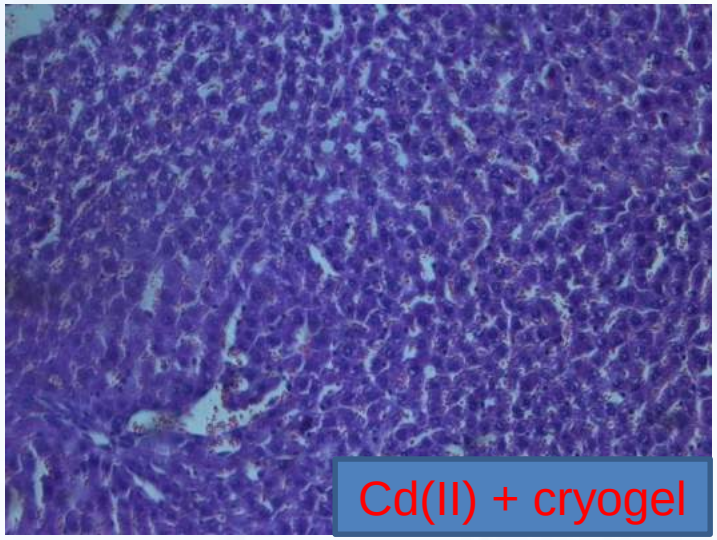
Metal	Dose	loading
$Cd(NO_3)_2$	LD_{50}	300 mg/kg
$CsNO_3$	LD_{50}	2390 mg/kg
$Sr(NO_3)_2$	LD_{50}	1982 mg/kg
$HgCl_2$	LD_{50}	75 mg/kg

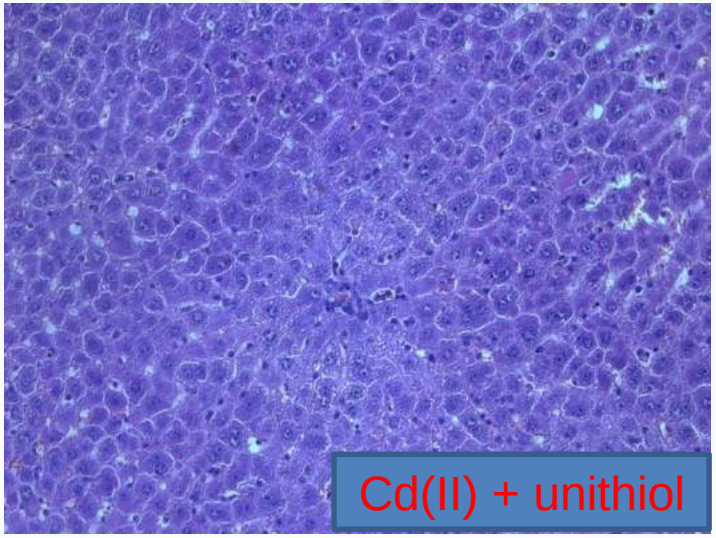


Cd(II) LD_{50} - section of liver

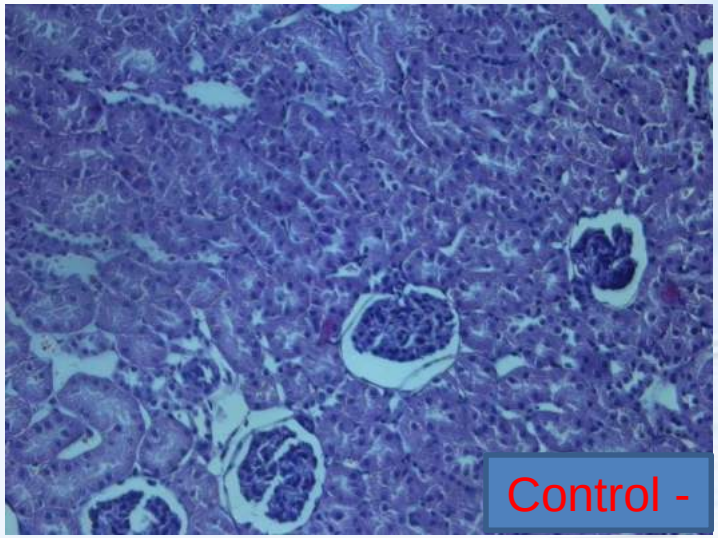


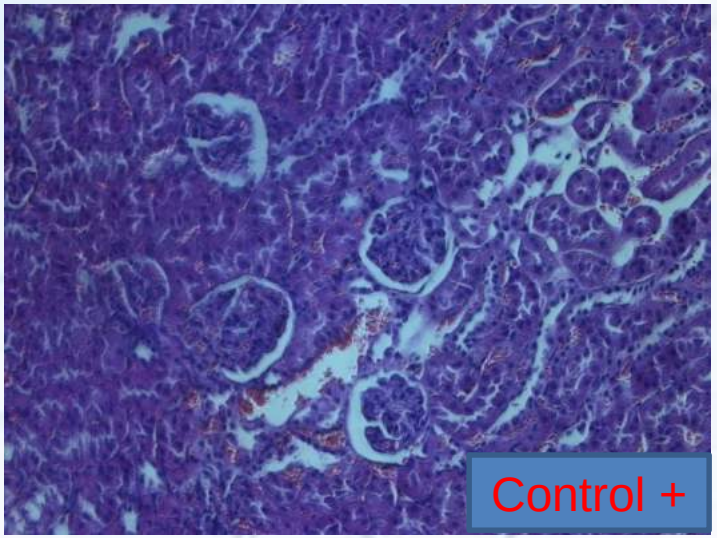




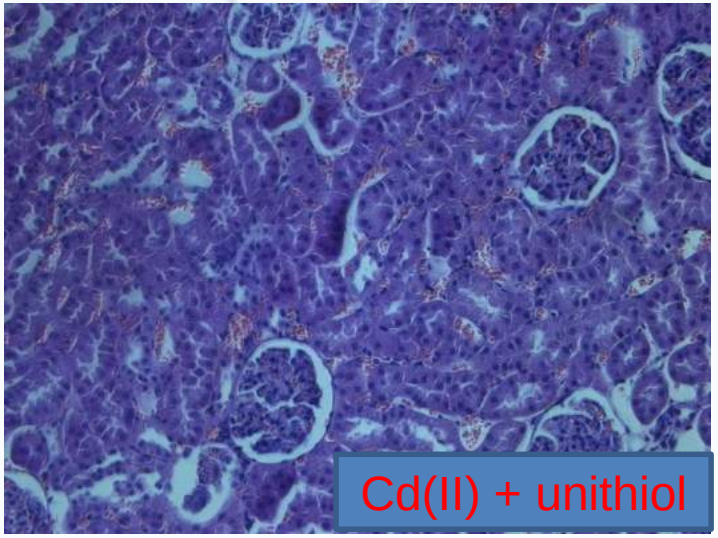


Cd(II) LD_{50} – section of kidney

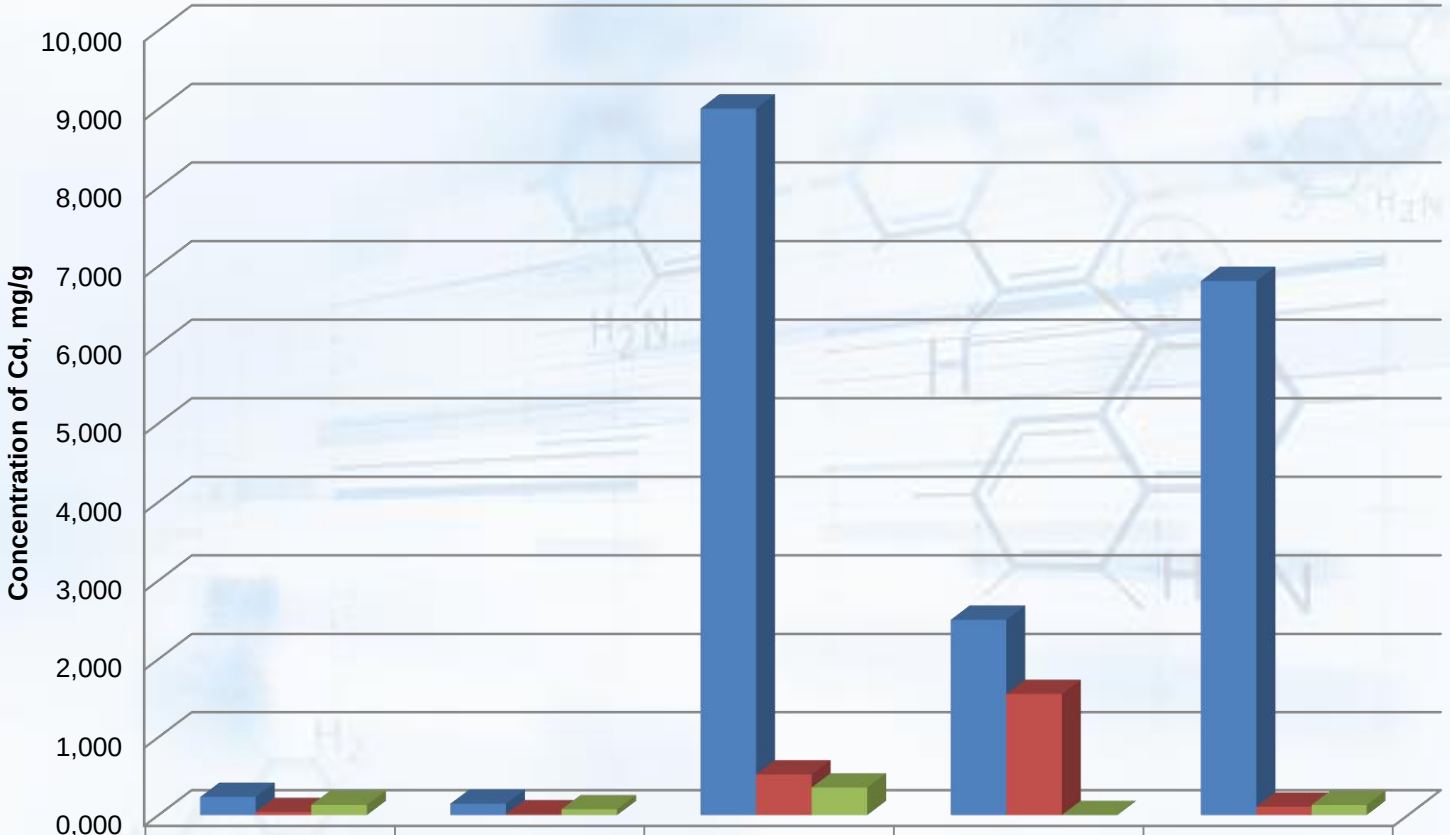






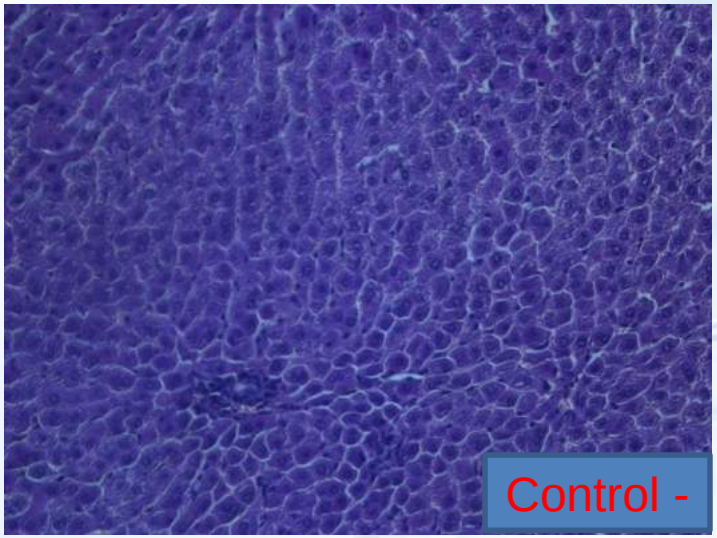


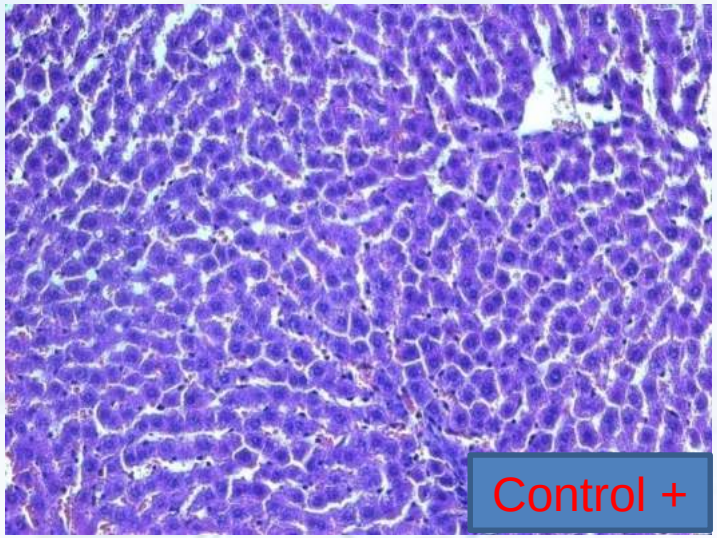
Residual concentration of Cd(II) in animal organs

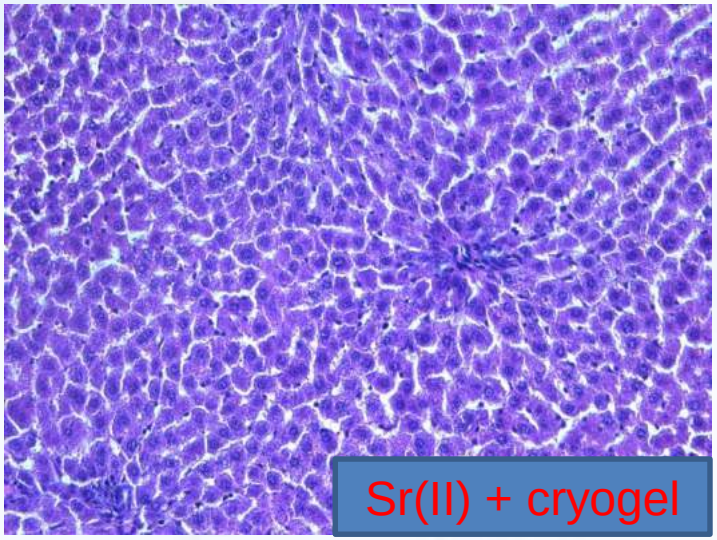


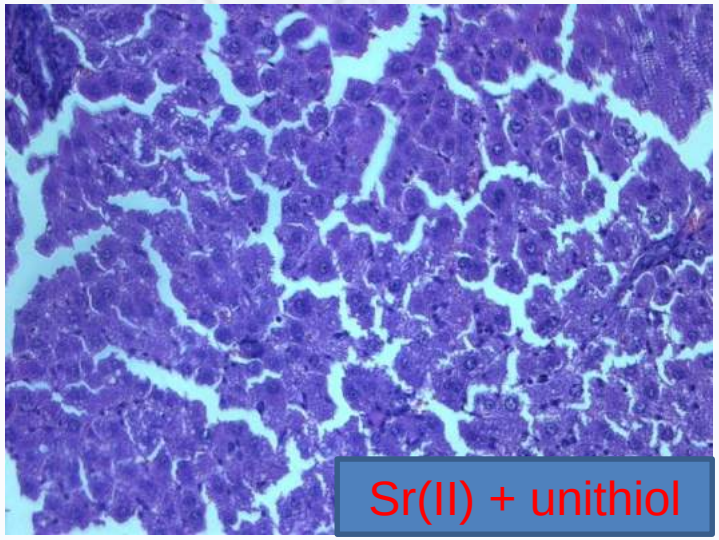
	Liver, mg/g	Kidney, mg/g	Stomack, mg/g	Omentum, mg/g	Duodenum, mg/g
Control+	0,234	0,146	9,007	2,500	6,812
ACd10	0,040	0,010	0,522	1,554	0,107
UCd47	0,131	0,075	0,354	0,002	0,129

Sr(II) LD_{50} - section of liver

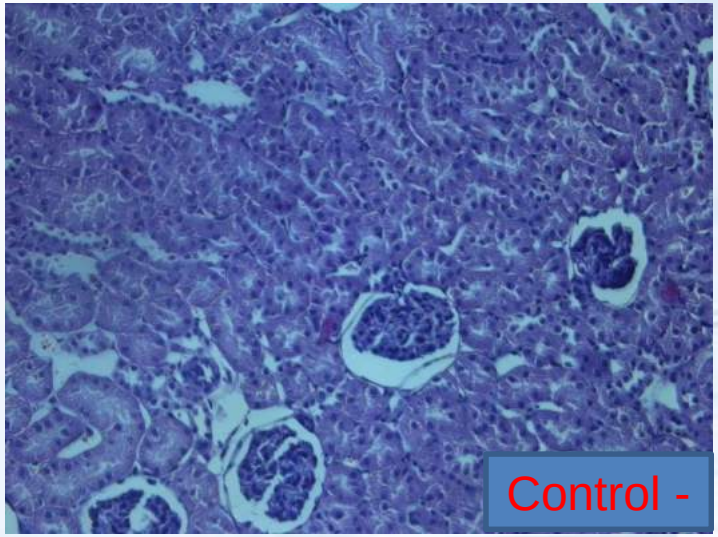


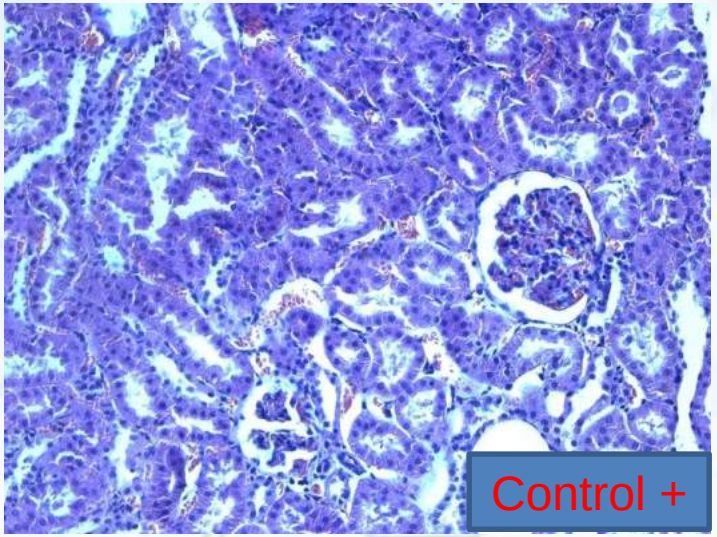


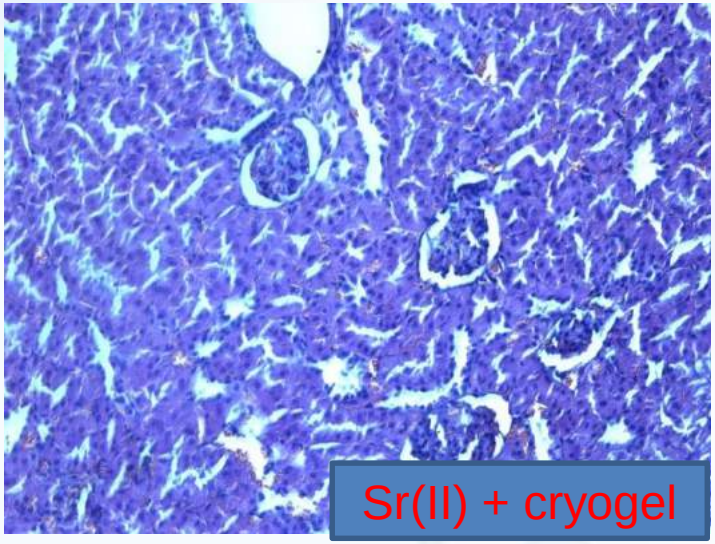


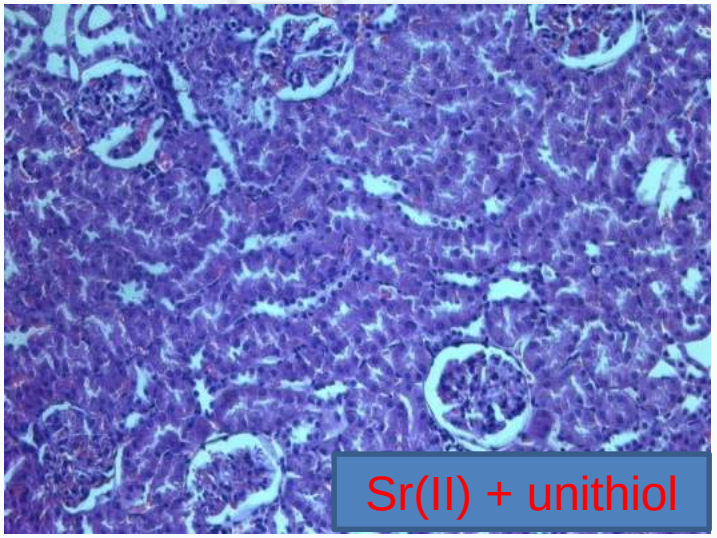


Sr(II) LD_{50} - section of kidney

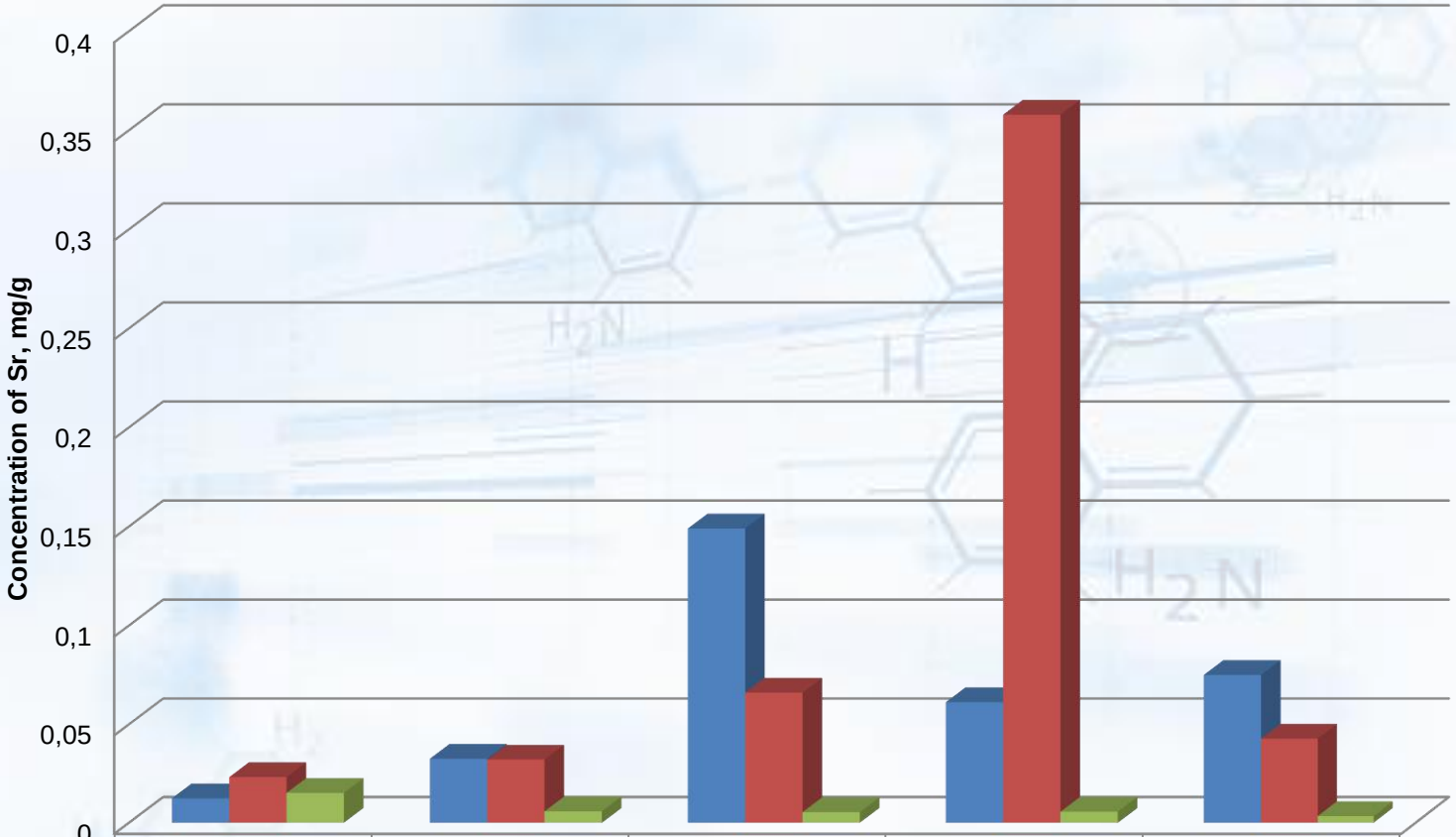






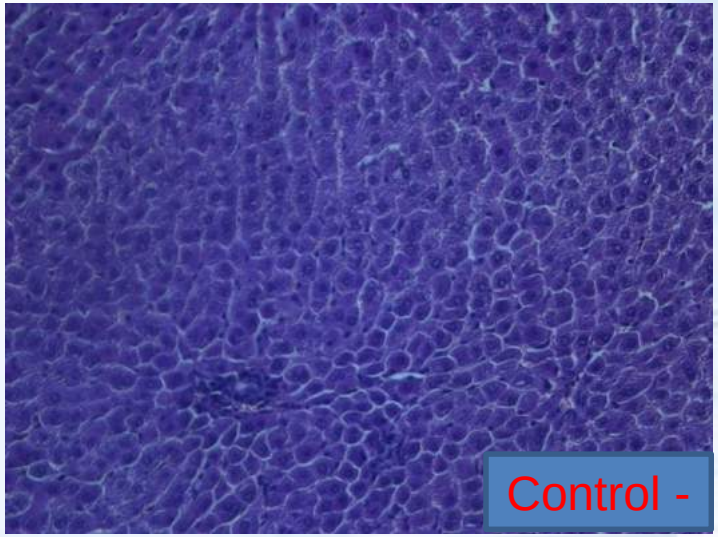


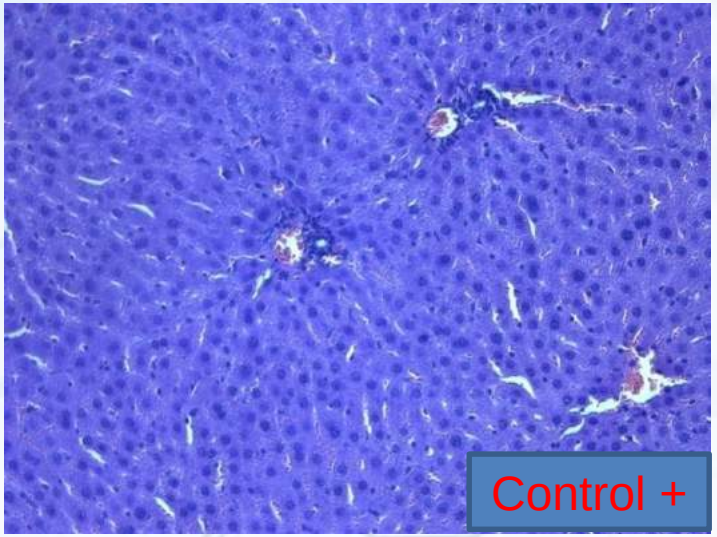
Residual concentration of Sr(II) in animal organs

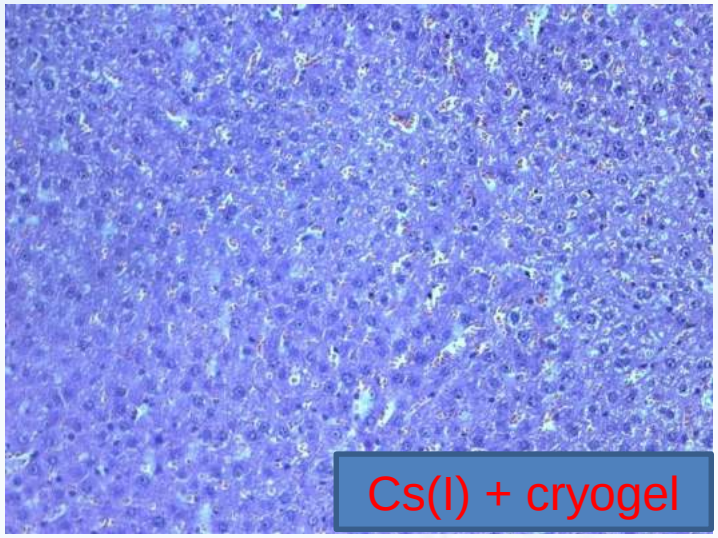


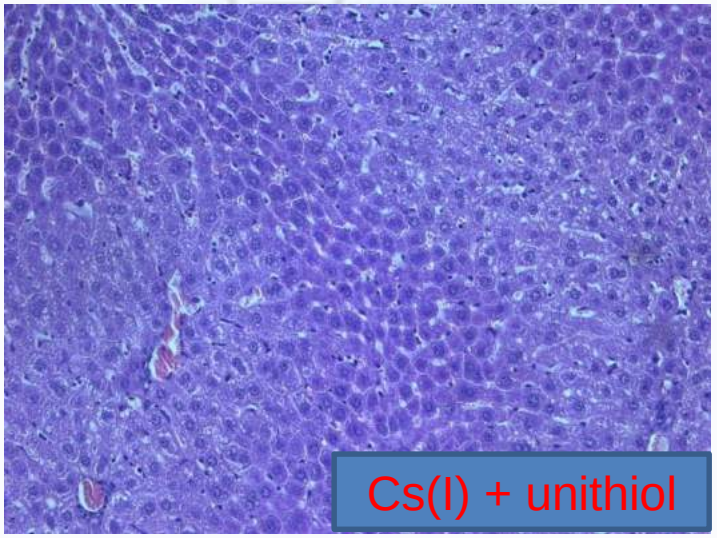
	Liver, mg/g	Kidney, mg/g	Stomack, mg/g	Omentum, mg/g	Duodenum, mg/g
Control+	0,0124	0,032517061	0,148974868	0,06125	0,075070822
BSr19	0,0232	0,032065023	0,066070137	0,357850421	0,042732558
USr50	0,0151848	0,005825	0,0054	0,005625	0,0034

Cs(I) LD_{50} - section of liver

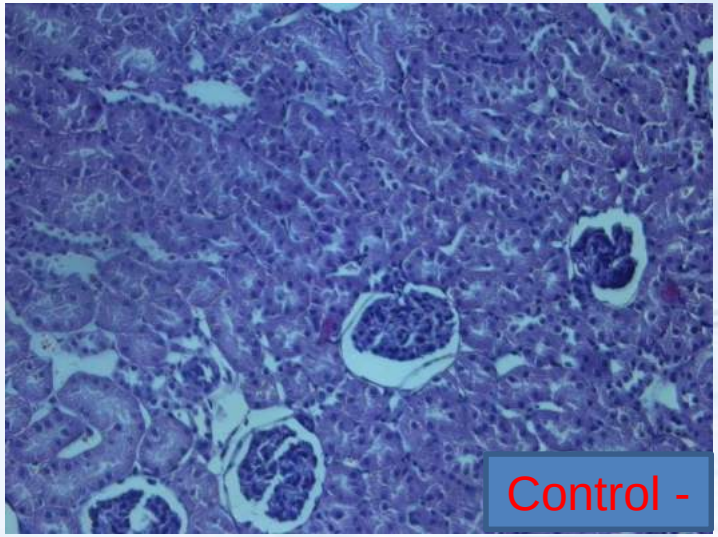


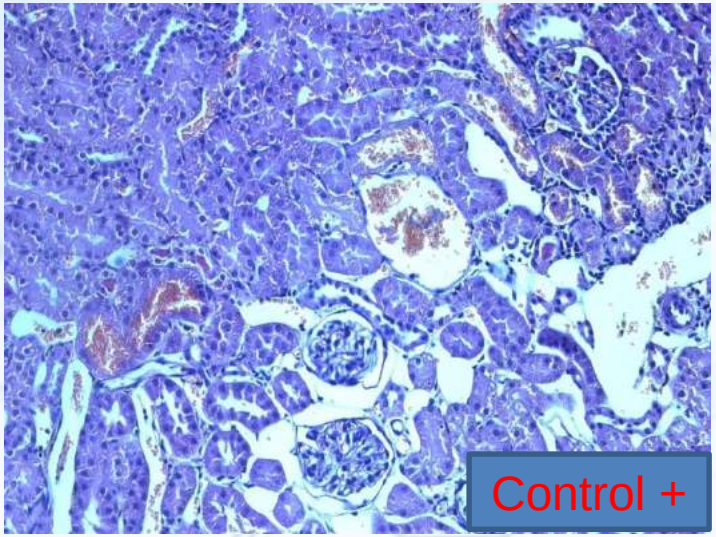


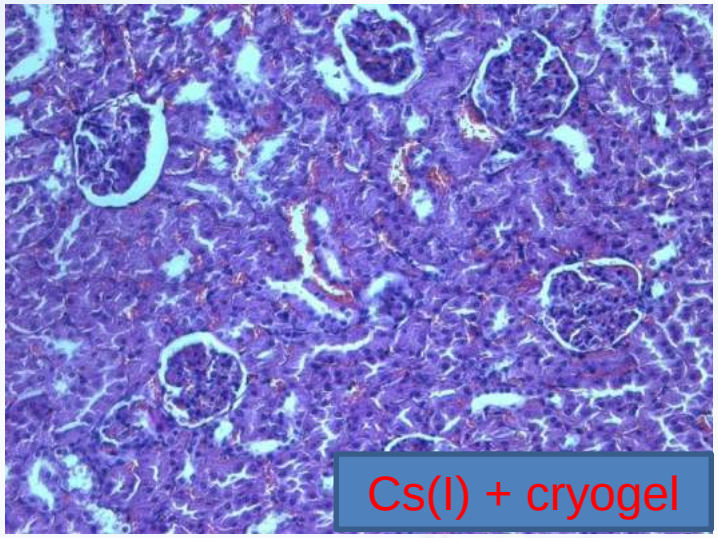


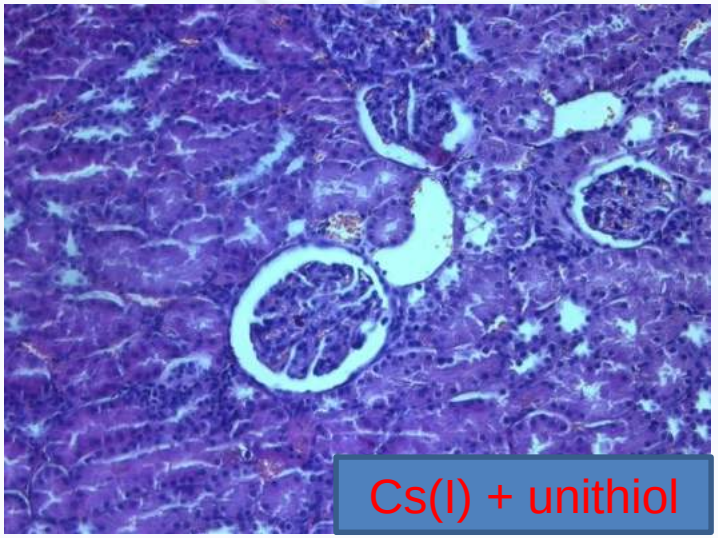


Cs(I) LD_{50} - section of kidney

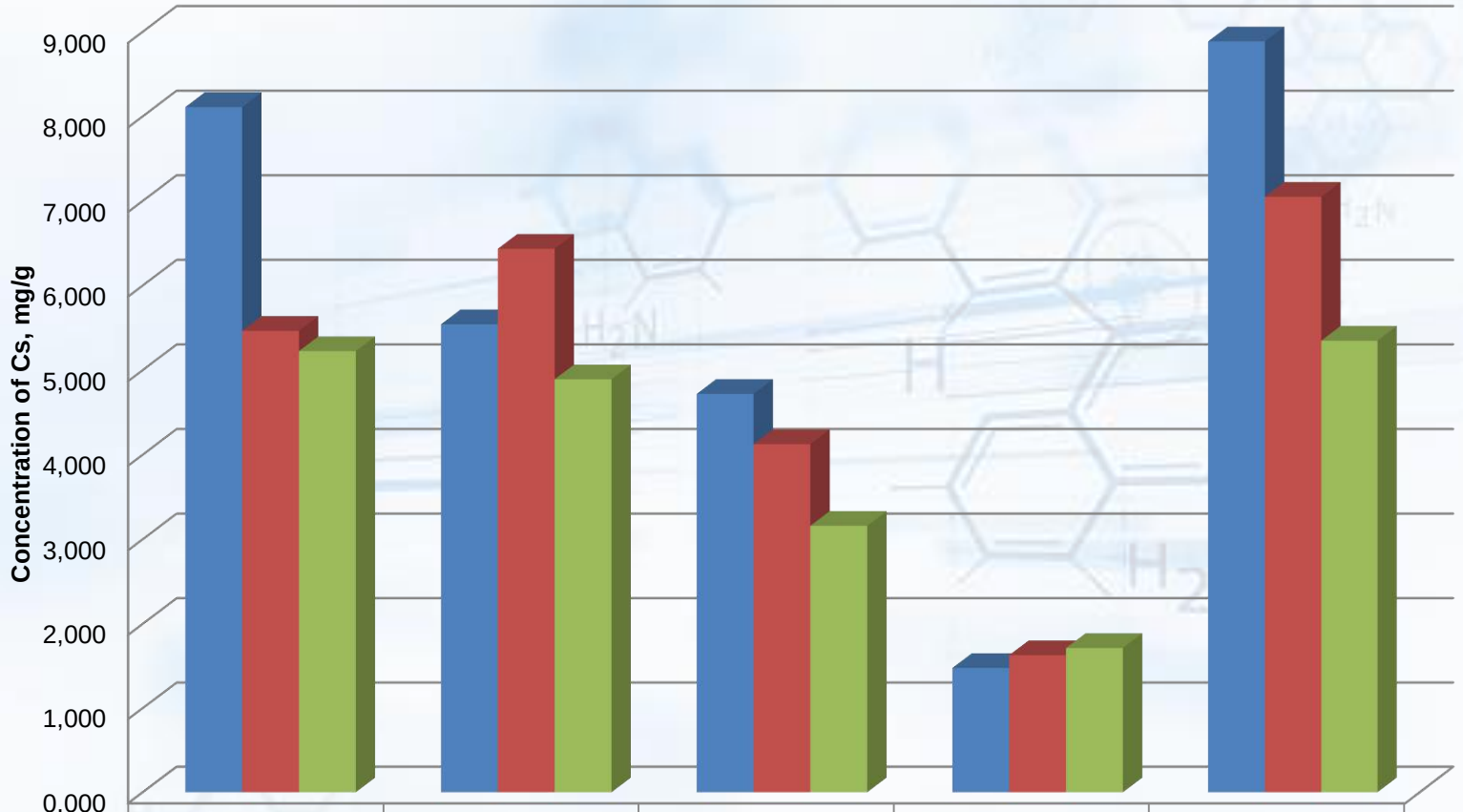






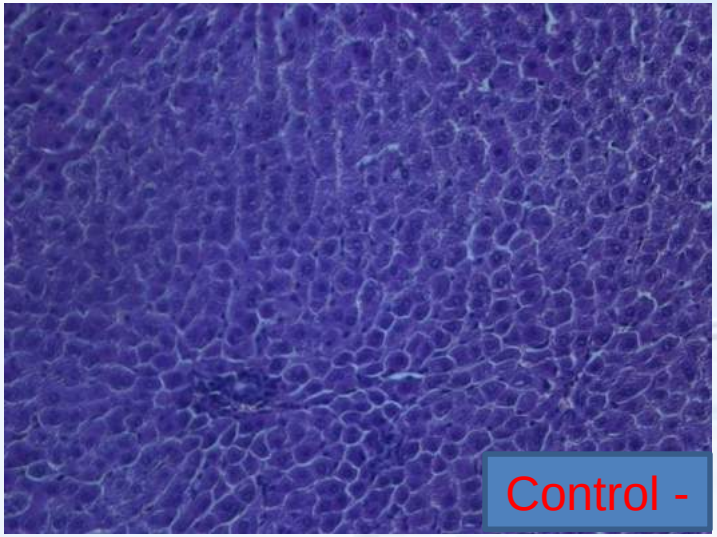


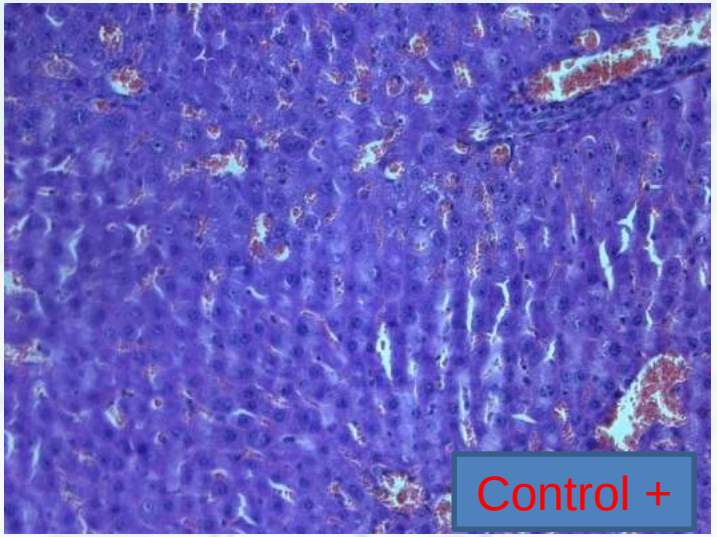
Residual concentration of Cs(I) in animal organs

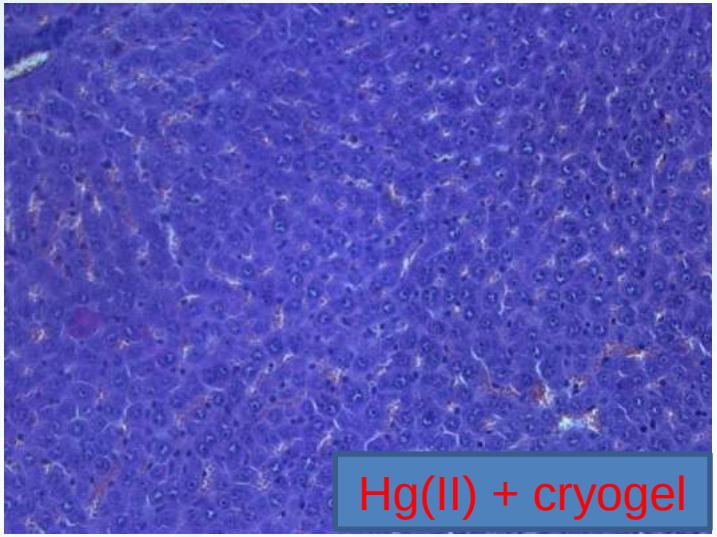


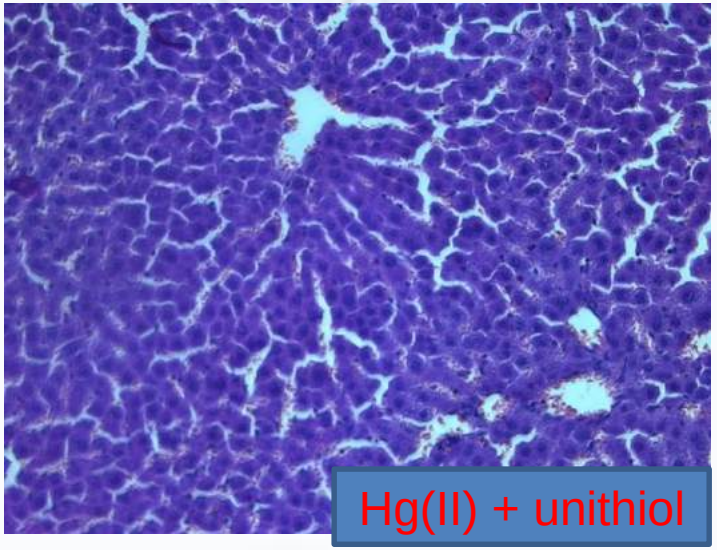
	Liver, mg/g	Kidney, mg/g	Stomack, mg/g	Omentum, mg/g	Duodenum, mg/g
Control+	8,110	5,542	4,719	1,478	8,887
BCs33	5,465	6,435	4,125	1,630	7,049
UCs54	5,225	4,891	3,159	1,715	5,348

Hg(II) LD_{50} - section of liver

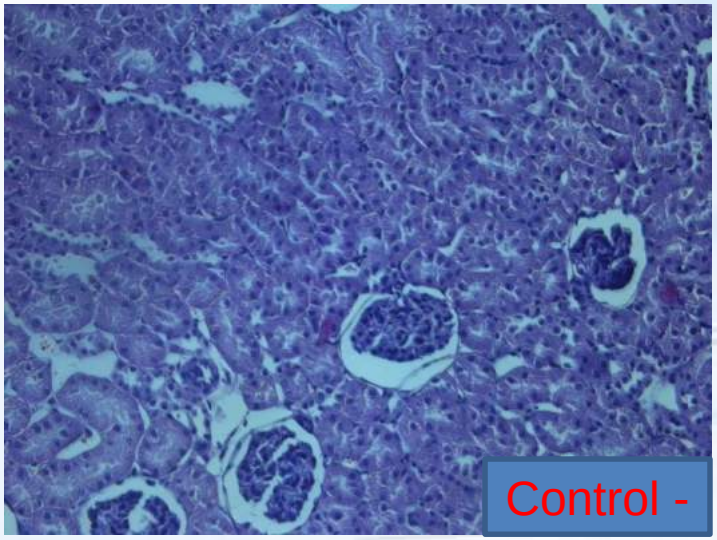


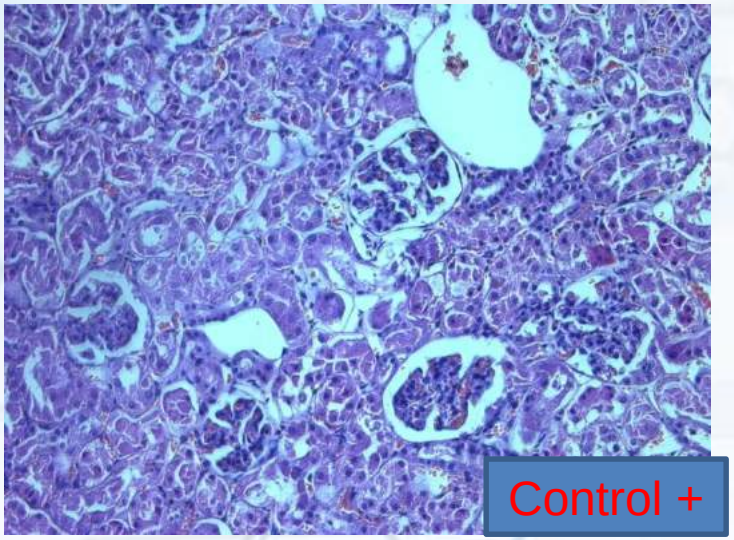


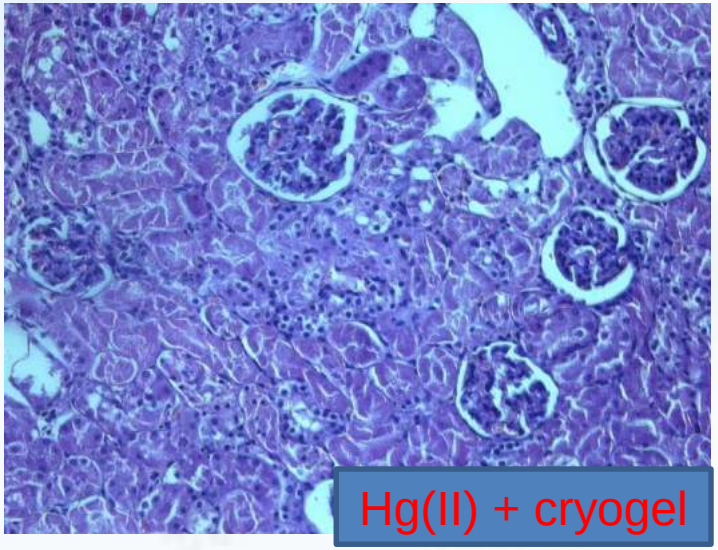


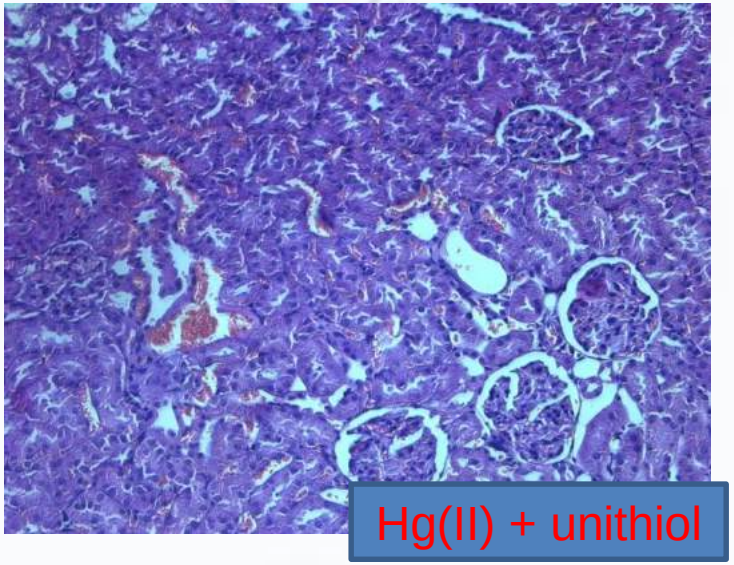


Hg(II) LD_{50} - section of kidney

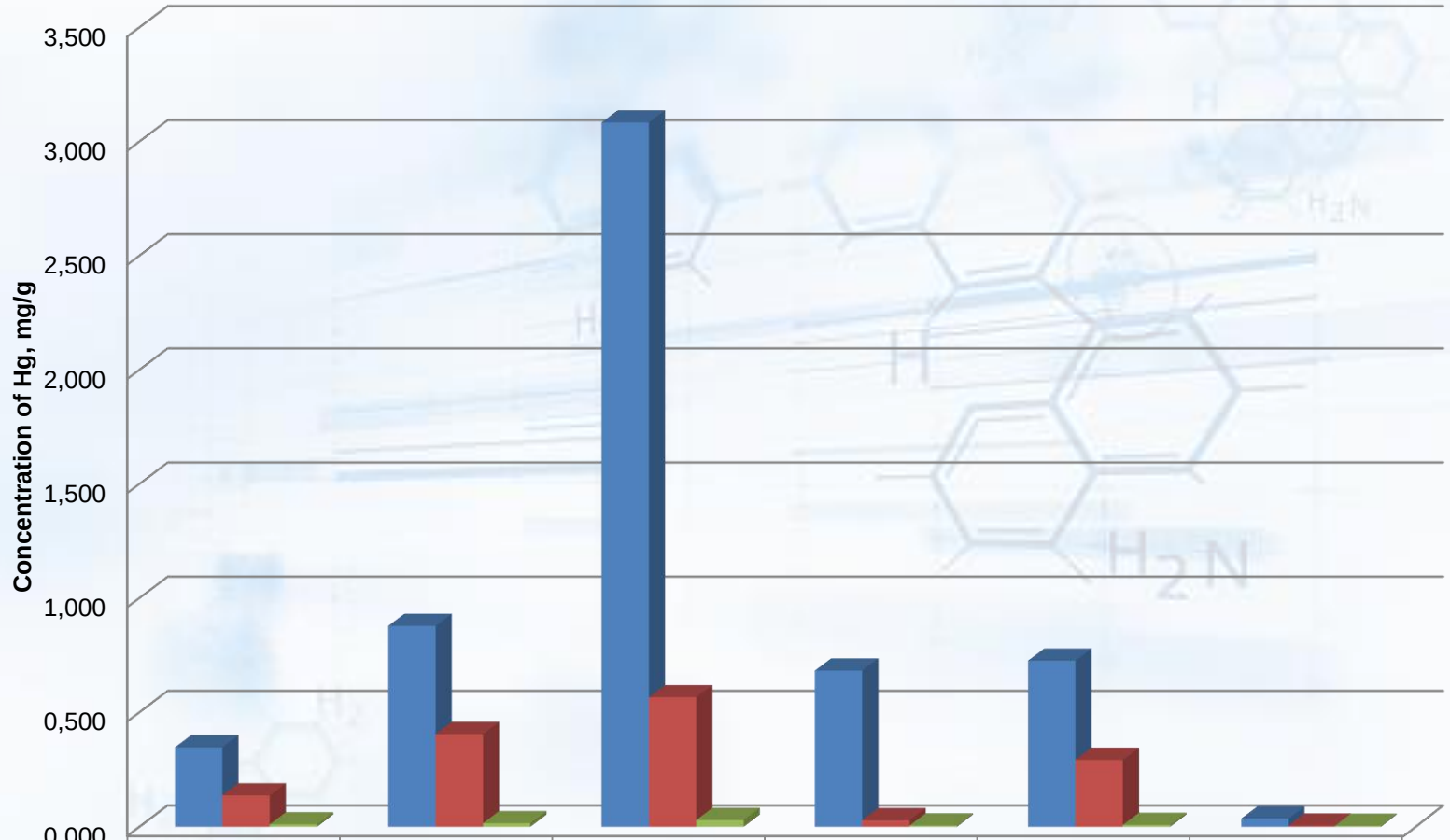








Residual concentration of Hg(II) in animal organs



	Liver, mg/g	Kidney, mg/g	Stomack, mg/g	Omentum, mg/g	Duodenum, mg/g	Brain, mg/g
Control+	0,347	0,878	3,083	0,682	0,725	0,036
AHg37	0,137	0,405	0,565	0,029	0,292	0,005
UHg57	0,011	0,016	0,030	0,006	0,008	0,004

Conclusion

• Macroporous cryogels based on N,N-dimethyl acrylamide, methacrylic acid and allylamine, crosslinked by N,N-methylenebisacrylamide were synthesized by free-radical polymerization in cryo-conditions.

• Surface characterization of laboratory synthesized cryogel showed that the material exhibited developed supermacroporosity, good elasticity and active ion-exchange ions which can be used as a heavy metal adsorbent.

• The maximum adsorption capacity for Cd(II) and Sr(II) was up to 450 mg/g of cryogel, Cs(I) up to 220 mg/g and for Hg(II) was approximately 250 mg/g.

• The results of animal experiments revealed that synthesized cryogels able to decrease the LD50 dose of metal ions from animal body and increase survival rate.

Thanks for your attention!

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Environmental Science & Technology Group