A XXXV-a **Conferinta** Nationala de **Chimie** - Caciulata, 02-05 octombrie **2018**

Detection of cadmium ions at glassy carbon electrodes modified with ordered mesoporous silica

Liana Maria Muresan[1]*, Ana-Maria Sacara[1], Graziella Turdean[1], Andrea Salis[2]

[1*]Babes-Bolyai" University, Department of Physical Chemistry, Cluj-Napoca, Romania

limur@chem.ubbcluj.ro

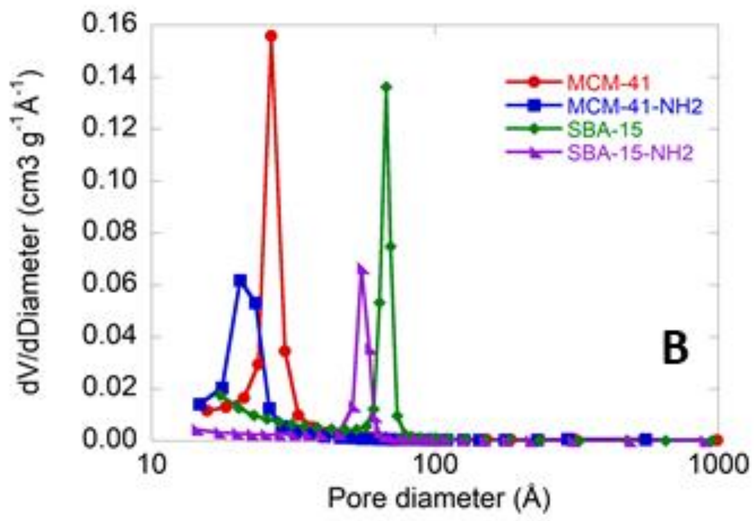
[2]Università degli Studi di Cagliari, CSGI, and CNBS, Dipartimento di Scienze Chimiche e Geologiche, Italy

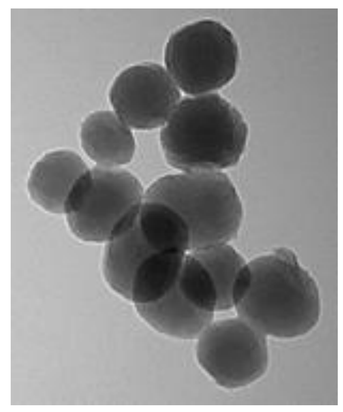
Electrochemical detection of Cd(II) has great potential for environmental monitoring of toxic metal ions due to the portability of electrodes and their excellent detection limits. Four sorts of ordered mesoporous silica (OMS) belonging to two different classes were used to prepare modified glassy carbon electrodes coated with Nafion in order to be used for the electrochemical detection of Cd(II) ions. The influence of NH2 functional group grafted on the OMS on the electrochemical response of the modified electrodes was investigated by using square wave anodic stripping voltammetry (SWASV) at two pH values (6 and 4.4).

Characteristics of the ordered mesoporous silica samples

Sample	S_{BET} (m^2/g)	$d_{Des,BJH}$ (nm)	$V_{pDes,BJH}$ (cm^3/g)	a (nm)
MCM-41	1168.6	2.26	0.80	4.01
MCM-41-NH_2	1030.0	2.40	0.75	4.35
SBA-15	880	6.7	1.25	11.7
SBA-15-NH_2	373	5.5	0.65	11.9

[a] Specific surface area calculated by the BET method. [b] Pore diameter calculated by applying BJH method to the data of the desorption branch. [c] Cumulative pore volume. [d] Lattice parameter obtained by SAXS



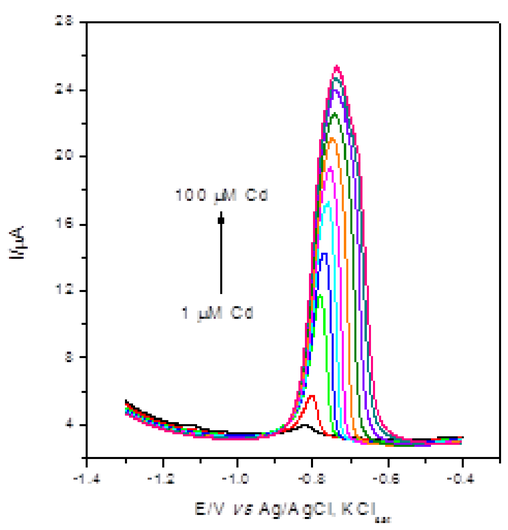


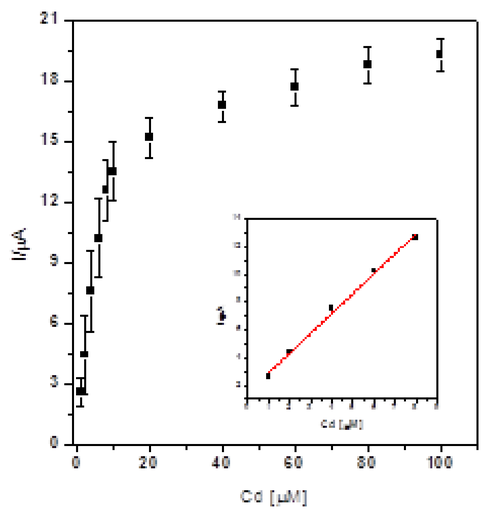
Pore size distributions and TEM image of silica

Preparation of GC/silica/Nafion modified electrodes

Silica suspensions were prepared using Sodium dodecyl sulphate (SDS) to obtain a homogenous suspension and to prevent precipitation. The suspensions (5 µL) were applied by drop-casting on the glassy carbon electrode's active surface and dried. To improve stability, a coating with 5 µl of 0.5% Nafion was created using the same method.

Square wave anodic striping voltammetry (SWASV)





SWASV measurements for Cd(II) detection at **GC/SBA-15-NH_2/Nafion** modified electrodes in phosphate buffer of pH 6 (left) and the corresponding calibration curves (right). Inset: linear region of the polarization curve.

Cd(II) /mM		Recovery (%)
GC/SBA-15-NH_2/Nafion	F-AAS	
9.25 ± 0.16	9.43 ± 0.09	98.09 ± 2.28

Electroanalytical parameters for silica modified GC electrodes

Electrode	Sensitivity (A/M)		Detection limit (µM)		Linear domain (µM)		R^2/no. of points	
	pH 6	pH 4.4	pH 6	pH 4.4	pH 6	pH 4.4	pH 6	pH 4.4
GC/Nafion	0.013 ± 0.001	0.165 ± 0.049	4.79	4.14	0 - 100	0 - 10	0.9987/12	0.9914/7
GC/SBA-15/Nafion	0.389 ± 0.013	0.564 ± 0.023	1.10	0.94	0 -10	0 -10	0.9942/7	0.9920/7
GC/SBA-15-NH_2/Nafion	1.483 ± 0.047	1.462 ± 0.052	0.66	0.73	0 - 8	0 - 8	0.9960/6	0.9950/6
GC/MCM-41/Nafion	0.633± 0.040	2.553 ± 0.098	1.32	0.51	0 - 6	0 - 8	0.9963/5	0.9942/6
GC/MCM-41-NH_2/Nafion	0.703 ± 0.030	2.716 ± 0.099	1.18	0.49	0 -10	0 - 6	0.9909/7	0.9901/5

•The large specific surface area of silica powders plays an important role in the electrodes performance. In some cases, the most important role is played by the -NH_2 groups, which have a beneficial effect, most probably due to the complexation possibility of Cd(II).

The authors acknowledge the UBB financial support from grants AGC30524 and AGC30805/2018.