New nanocomposites based on silica and the growth substrate of Pleurotus ostreatus with applications in adsorption processes

Research article

Andreea Eliescu[1]*, Nicoleta Cioateră[1], Mihaela Mureșeanu[1]

[1] University of Craiova, Faculty of Sciences, Department of Chemistry, Calea Bucuresti, 107i, Craiova, Romania
*E-mail: andreea200752@yahoo.com

Abstract

The present study aimed at the synthesis and characterization of new biosorbents by modifying the POBM (growth substrate of the macromycete *Pleurotus ostreatus*) using a commercial silica (DAVICAT 1452) in order to improve the absorbtion properties and the thermal, chemical and mechanical stability of the biosorbents which were presented in a previous study. In order to select the sorbent with the best performance, nanocomposites based on silica and biomass were obtained by different methods. The efficiency of the materials was tested for the removal of Cd(II) ions from aqueous solutions. The maximum capacity and rate of adsorption were for the biosorbent calcinated at 550^0C after material synthesis and they were comparable with similar materials presented in the specialised literature.

1. INTRODUCTION

In adsorption technology, inorganic materials are widely used due to both their chemical and thermal stability and their regenerative capacity. A variety of metal oxides such as iron, nickel, magnesium, zinc, manganese, copper, titanium or silicon oxides have been used to remove contaminants from water [1].

Silica-based nanomaterials have great potential in metal ion adsorption due to their unique characteristics such as large, controllable surface area and well-defined pore size [2]. In addition, nanosilica is a non-toxic and environmentally friendly adsorbent. Modified silica, on the other hand, has a better capacity for the adsorption of acid dyes and heavy metal ions [3], showing stronger interactions with the adsorbate [4]. Functional groups on the surface increase the mechanical strength and adsorption capacity of silica [5]. Among them, amino groups have been widely used to modify the surface of silica so that functionalized silica can remove both cationic and anionic contaminants from water. Protonated amino groups adsorb anionic pollutants by electrostatic attraction at low pH [6], while at high pH they can remove cationic pollutants such as heavy metals [7].

Biomass has been widely used as an adsorbent material, being converted to activated carbon by high-temperature carbonization or pyrolysis, or by shredding the dry biomass and sieving the resulting powder to suitable particle sizes for adsorption studies [8]. Although biomass in its native form has proven to be a suitable adsorbent, it has a low adsorption capacity, which limits its practical application.

To increase the adsorption capacity, various composites have been fabricated with the aim of removing contaminants more efficiently. Metal oxide nanomaterials together with their composites show enormous potential for the rapid and efficient removal of contaminants from wastewater due to the control of their morphological and textural properties, crystalline nature and availability [9-11].

In a previous study we presented the adsorbtive properties for Cd(II) ions of the growth substrate of the macromycete *Pleurotus ostreatus* and the maximum adsorption capacity for an initial concentration of 50 mg/L was 3.58 mg/g. In order to improve the

absorbtion capacity and the thermal, chemical and mechanical stability, new nanacomposites based on the above biomass and silica nanoparticles have been synthesized. As silica source, we used commercial DAVICAT silica nanoparticles. The synthesis method involved either biomass or the final composite to be calcinated at different temperatures. The obtained materials were tested for Cd(II) adsorption in order to select the best biosorbent.

2. MATERIALS AND METHODS

2.1. Biocomposite synthesis

The experimental protocol was adapted from literature [12] and consisted in dispersing 1.0 g of DAVICAT 1452 silica nanoparticles (a commercial silica obtained from Grace-Davison, with a particle size of 200 μm, a specific surface area of 390 m^2/g, a pore volume of 1.1 mL/g and a pore diameter of 10 nm) in a mixture of 25 mL of ethanol and 25 mL of water under magnetic stirring. *Pleurotus ostreatus* spent substrat (POBM) samples were rinsed with distilled water and oven-dried at 40 ± 2^0C for a period of 48 h to constant weight, followed by 40.0 mesh sieving and autoclave treatment for 15 min at 121^0C in order to inactivate the biomass and allowing to be stored in optimal conditions. 5 g of POBM biomass was added and stirring was continued for 90 min, so the mass ratio between the two components was 1 SiO_2/5 POBM. The resulting mixture was transferred to an ultrasonic bath where it was maintained for 4h. After that it was separated by centrifugation (5 minutes at 4000 rpm), washed twice with 10 mL of water, centrifuged again and dried in an oven [7]. The nanocomposites (3.7 g), further noted POBM_DAVICAT_S (uncalcined sample), were obtained with a yield of η=61.66%. Following the same procedure, samples POBM_250_DAVICAT_S (with biomass calcined at 250^0C), POBM_DAVICAT_S_250 (nanocomposite calcined at 250^0C) and POBM_DAVICAT_S_550 (nanocomposite calcined at 550^0C) were synthesised.

2.2. Characterization techniques

The materials were characterized with the following equipment:

- Rigaku SmartLab X-ray diffractometer with CuKα radiation (λ = 1.5406 Å), in the range 2θ= 5-80º to obtain the X-ray diffractograms
- Bruker Alpha spectrophotometer for recording FTIR spectra in the range 4000-400 cm^{-1}
- Hitachi SU8010 scanning electron microscope for determining textural, morphological properties and elemental composition of samples
- Automatic Quantachrome analyzer for the determination of specific surface area and porosity parameters
- NETZSCH STA 449F3 thermogravimetric analyzer for thermal degradation of samples in the temperature range 20-1000^{0}C, in an aluminum crucible, with a temperature increase rate of 10^{0}C/min under N$_2$ atmosphere
- GBC Avanta flame atomic absorption spectrometer (FAAS) equipped with air-acetylene flame for determination of Cd(II) content of samples

2.3. Sorption experiments of metal ions

A 1000 ppm Cd(II) stock solution was prepared in deionized water using cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$.4H$_2$O). The adsorption experiments were carried out in batch mode, in polypropylene vessels that contained 0.1 g of biosorbent and 50 mL of 50 mg/L Cd(II) solution. In order to make a comparison between the adsorption capacity of POBM biomass (tested in a previous study) and that of the new composite, we worked at a pH value of 5, determined as the optimal value for maximum adsorption. Also, the isoelectric pH of the composite was determined as having the value of 4.92 compared to the value of 6.77 determined for POBM [13]. The solutions were mixed by mechanical stirring for 2 h, after which they were filtered using syringe filters, and the concentration of metal ions was determined by FAAS spectrometer.

The maximum adsorption capacity and percentage removal of metal ions were calculated using the following equations:

$$q_e = \frac{V(C_0 - C_e)}{m}$$ (1)

(2)

$$R\% = \frac{C_i - C_f}{C_i} \times 100$$

where: q_e represents the equilibrium sorption capacity measured in mg/g, V is the volume of the aqueous phase in L, m is the amount of sorbent expressed in g, and C_0 and C_e are the initial concentration of the metal ion in the aqueous phase, respectively the concentration at equilibrium (mg/L).

3. RESULTS AND DISCUSSION

3.1. Structural, textural and morphological properties of the synthesized materials

The new-synthesized nanocomposites based on silica nanospheres and POBM biomass were characterized using various techniques including SEM, EDX, FTIR and XRD.

The shape, size, morphology and elemental composition for POBM biomass, DAVICAT silica nanoparticles and POBM_DAVICAT composites were examined by SEM analysis coupled with EDX.

The SEM images shown in Figure 1 demonstrate that POBM has a typical texture for biomass, with an irregular, compact surface.

The nanostructured DAVICAT silica morphology is as spherical particles with average diameters between 100-300 nm, which undergo an agglomeration process. This agglomeration occurs due to the network of three-dimensional hydrophilic groups $-Si(OH)_2-O-Si(OH)_2-$ on the silica surface.

The composite samples POBM_DAVICAT_S, POBM_250_DAVICAT_S and POBM_SiO_2_DAVICAT_550 show

aggregates of spherical shape. The average particle size is about 250 nm. These were probably formed by the deposition of silica nanoparticles preferentially on the surface of the cell wall of cellulosic structures of the biomass.

Taking into account that the mass ratio between DAVICAT silica and biomass is 1/5, it is possible that the excess of biomass that does not enter into the composite nanospheres leads to their agglomeration.

In these heterogeneous structures there are portions of biomass not covered with silica. In the case of nanocomposites calcined at 550^0C, a morphology similar to that of silica nanospheres is observed, but with lower degree of agglomeration and amorphization, as it can be seen from the X-ray diffractograms (Figure 4).

According to the EDX analysis (Table 1) the corresponding atomic percentages of C, O and Si were 54.57%, 40.15% and 10.50% for the uncalcined composite; 45.34%, 37.59% and 15,9%; for the composite with biomass sample calcined at 250^0C; 34.23%, 35.83% and 27.77% for the composite calcined at 550^0C.

In the case of POBM_250_DAVICAT_S, the use of biomass calcined at 250^0C led to a decrease in the percentages of C and O and an increase in the percentage of silicon, which indicates a higher amount of silica in the final composite.
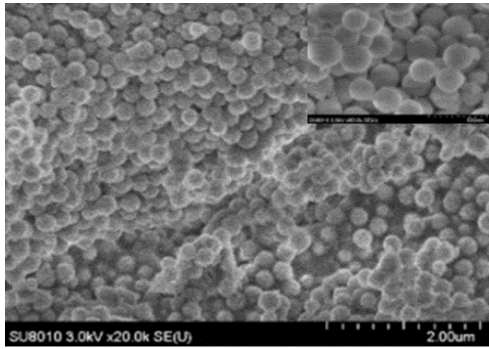
By biomass calcination, either an amount of organic matter was lost or a larger number of functional groups were presented on its surface. These effects probably allowed more interactions with the inorganic component that was better retained in the composite structure.
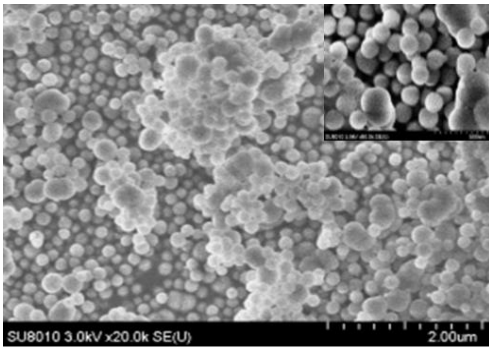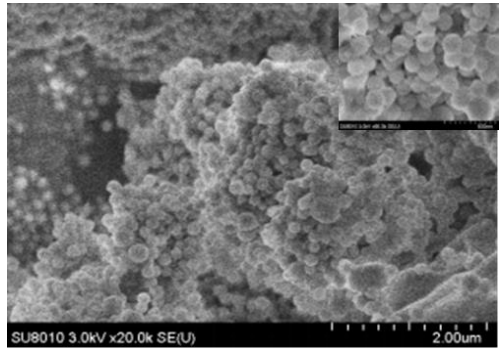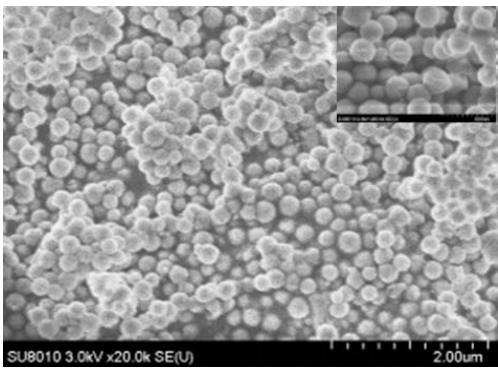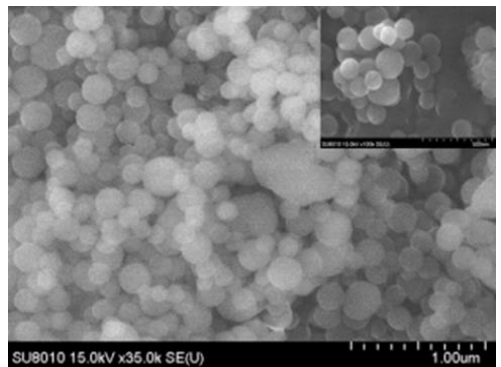
DAVICAT SILICA
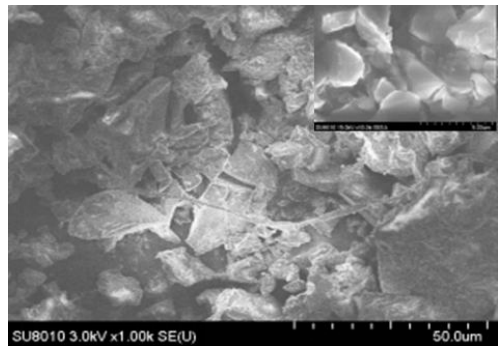
POBM_250

POBM_DAVICAT_S

POBM_250_DAVICAT_S

POBM_DAVICAT_S_550

POBM_250_DAVICAT_S_Cd

Figure 1. SEM images of the tested materials

For the composite calcined at a temperature of 550°C, the same effect was observed, with a more significant increase in the percentage of silicon. This effect may be due to a better structuring of the silica during calcination and the formation of more bonds with the organic matter of the POBM biomass. It is also possible that some of the organic

components were degradated during calcination and were lost as final degradation compounds, CO_2 and H_2O. There is also a slight decrease in the percentage of Si in nanocomposites compared to silica, which highlighted the active participation of Si-OH groups in interactions with the organic components. Elements such as P, K, Mg or Ca were also presented after the incorporation of the silica into the POBM biomass, indicating the formation of the corresponding nanocomposites [13]. After the interaction of Cd with the POBM_250_DAVICAT_S composite material, the percentages of C, O, and Si were 50.55%, 22.46%, and 24.69%, respectively. The appearance of a signal corresponding to Cd in the EDX spectrum (Figure 2) confirmed the adsorption of Cd(II) ions on the surface of the composite. In addition, the reduction of O percentages and the increase of Si and C percentages supported a greater participation of oxygenated organic groups on the surface of the POBM organic component (-COOH, C_6H_5-OH, -OH) in the adsorption of Cd (II) ions compared to the siloxane network of silica.
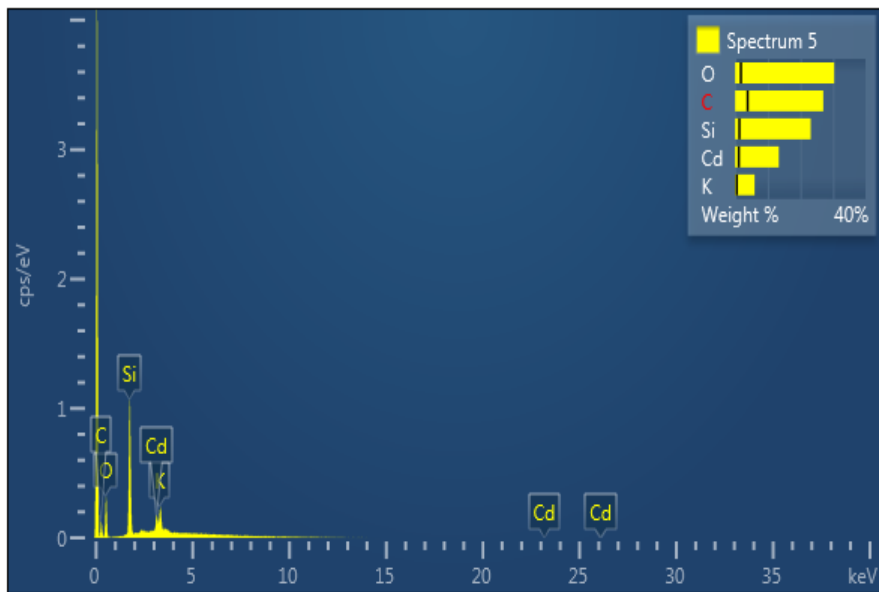

Figure 2. EDX spectra of the POBM_250_DAVICAT_S_Cd sample

Table 1. Elemental analysis of composites with POBM and silica

Atomic percent	SiO$_2$	POBM_250	POBM_ DAVICAT_S	POBM_250_ DAVICAT_S	POBM_250_ DAVICAT_S_Cd	POBM_DAVICAT_ S_550
C (%)		78,14	54,57	45,34	50,55	34,23
O (%)	76,15	18,84	40,15	37,59	22,46	35,83
Si (%)	22,23	1,10	10,50	15,98	24,69	27,77
Na(%)	0,96	0,13	2,03	-	-	-
S (%)	0,77	0,06	0,12	-	1,72	-
P (%)		0,11		-	-	1,18
K (%)		1,43		0,96	1,25	1,99
Mg(%)		0,10		-	-	-
Ca (%)	-	-		0,68	1,82	-
Cd(%)	-	-		-	0,50	-

The FTIR spectra analysis (Figure 3) was used to identify the main functional groups on the surface of the synthesized composite materials and their involvement in the adsorption of cadmium ions. The silica showed a band characteristic of the silanol groups in the range 3200-3400 cm^{-1}, a peak that can be attributed to the asymmetric stretching of the Si-O-Si bonds at about 1073 cm^{-1} and a signal at 791 cm^{-1} represented by the symmetric stretching of Si-O bonds [12]. As in the FTIR spectrum of POBM biomass [13], for the composites, the signal at 3200-3400 cm^{-1} can be attributed to -OH groups from pectin, lignin or carbohydrates, specific to polymer compounds from biomass as well as to silanol groups from silica. The absorption band appearing at 2800-2900 cm^{-1} is due to the symmetric and asymmetric stretching vibrations of the C-H bonds. A peak in the range 1500-1600 cm^{-1} was also observed for the stretching vibrations of the C=O bonds in the carboxylate ions. The peaks in the range 1050-1100 cm^{-1} indicated the stretching vibration of the Si-O-Si bonds due to the presence of silica in the composite samples. Thus, the signal that appeared at 1055 cm^{-1} and increased in intensity for the composite calcined at 550⁰C, could be attributed to the stretching of the Si-O-Si bond. Another signal appeared at 795 cm^{-1}, indicating the symmetric stretching vibrations of the Si-O-Si bonds, which were also observed in the FTIR spectra of the composites based on SiO_2 and orange peel biomass [10].
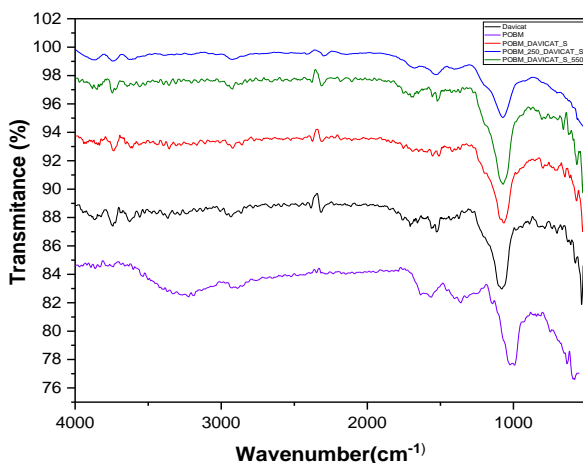

Figure 3. FTIR spectra of composites based on POBM and Davicat silica

In the X-ray diffractogram of the POBM biomass, an extended peak was identified in the range $2\theta=15°-30°$, representing the diffraction peak characteristic of cellulose, pointing out the amorphous nature of the biomass [9].

From figure 4, it can be seen that the silica presented a broad band with a maximum at $2\theta=22^0$, characteristic of amorphous silica, located in the same range as the characteristic peak of the biomass.

In the case of the nanocomposites, a diffraction peak was identified in the same 2θ domain with a lower intensity than for the Davicat silica, showing an increase in the degree of amorphization of the silica in the composite.

The distance between the planes of the pore network increased for all composites compared to Davicat silica particles.
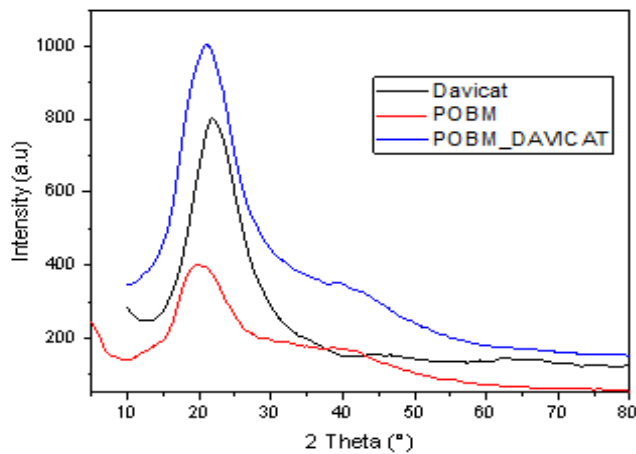

Figure 4. X-ray diffractograms of POBM, DAVICAT silica and the corresponding composite samples

3.2 Sorption studies of Cd (II) ions

In order to determine the maximum adsorption capacity,q_e, for the tested materials, sorption studies were done for Cd(II) ions from an

aqueous solution with 50 mg/L initial concentration. Firstly, all the synthesized materials presented a greater adsorption capacity in comparison with the POBM biomass and the DAVICAT silica, when these two sorbents were tested alone for Cd(II) adsorption. It should be noted that at this Cd concentration, the POBM biomass presented an adsorption of 3.58 mg/g, and the DAVICAT silica nanoparticles of 20 mg/g. As can be seen from Table 2, the highest sorption capacity for Cd(II) ions was for the nanocomposite calcinated at 550^0C, followed by that in which the biomass was calcinated at 250^0C before synthesis. These resuls could be correlated with the structural analysis that indicated a more well-ordered structure for the calcinated materials. Either for the materials with calcinated biomass or for those calcinated after synthesis, the EDX analysis revealed an increase of the silicon percent and a corresponding decrease of C% and O%, which correlated with a greater amount of silica and better interaction between the two components of the final composite. All these effects are beneficial for a better adsorption of the Cd(II) ion from aqueous solution.

Table 2. The sorption capacities of Cd(II) ions on the adsorbent materials tested at $C_i=50$ mg·L^{-1}

Sample	q_e/mg·g^{-1}
POBM_Davicat_S	2,89
POBM_250_Davicat_S	24,53
POBM_Davicat_S_250	9,08
POBM_Davicat_S_550	28,25

4. CONCLUSIONS

This study presented new composites obtained from the growth substrate of the macromycete *Pleurotus ostreatus* (POBM) and commercial DAVICAT silica nanospheres by different methods and their application as effective adsorbents for the separation of Cd(II) from polluted aqueous media. The morphology of the composite samples is in the form of aggregates of spherical nanoparticles with an average particle size distribution of approximately 250 nm. In order to improve the adsorption capacity, several methods of synthesis of

nanobiosorbents were used, namely calcination of the biomass prior the composite synthesis or calcination after its preparation. The maximum adsorption capacity at the tested concentration of Cd ions was 28.25 mg/g, superior to that of the individual components, biomass (3.58 mg/g) and silica (20 mg/g), respectively.

All these results, analyzed compared to similar materials presented as adsorbents for Cd(II) in the specialized literature, indicate the potential of using these new bioadsorbent composites for the effective removal of cadmium ions from polluted aqueous environments.

REFERENCES

[1] H.S. Kim, J.W.Lee, N. Yantara, P.P. Boix, S.A.Kulkarni, S. Mhaisalkar, M. Grätzel and N.G. Park, *Nano Lett.,* 13 **(2013)** 6.

[2] S. Ma, X. Zuo, J. Xiong, C. Ma and Z. Chen, *J. Water Process Eng*., 33 (**2020)** 10.

[3] S. Wadhawan, A. Jain, J. Nayyar and S.K. Mehta, *J. Water Process Eng*., 33 (**2020)** 2.

[4] X. Fu, X. Chen, J. Wang and J. Liu, *Microporous Mesoporous Mater*., 139 (**2011)** 1.

[5] H. Yang and Q. Feng, *Microporous Mesoporous Mater*., 135 (**2010)** 7.

[6] J. Aguado, J.M. Arsuaga, A. Arencibia, M. Lindo and V. Gasc'on, *J. Hazard. Mater*., 163 (**2009)** 1.

[7] Liberman, N. Mendez, W.C. Trogler and A.C. Kummel, *Surf. Sci. Rep*., 69 (**2014)** 2.

[8] M.F. Zayed, W.H.Eisa and B. Anis. *Desalin. Water Treat*., 57 **(2016)** 57.

[9] K.W.Jung, S.Y.Lee and Y.J.Lee, *Bioresour. Technol*., 260 **(2018)** 204.

[10] S.I.Siddiqui and S.A.Chaudhry, *J. Clean. Prod.,* 200 **(2018)** 996.

[11] X.Liu, F. Shen and X. Qi, *Sci. Total Environ*., 666 **(2019)** 694.

[12] J. Saini,V.K.Garg and R.K.Gupta, *Arabian Journal of Chemistry*, 13 (**2020)** 1.

[13] A.A. Georgescu, A. Eliescu, C.M. Nicolescu, M. Bumbac, N. Cioateră, M. Mureşeanu and L. C. Buruleanu, *Analytical Letters,* (**2019)** 13.