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SOFIA UNIVERSITY - MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

National Recovery and Resilience Plan
OF THE REPUBLIC OF BULGARIA

NEW COMPOSITE MATERIALS FOR SELECTIVE DETERMINATION OF TOXIC FORMS OF CHEMICAL ELEMENTS IN ENVIRONMENTAL SAMPLES

Research Problem: Ionic liquid modified polymer gel for arsenic speciation

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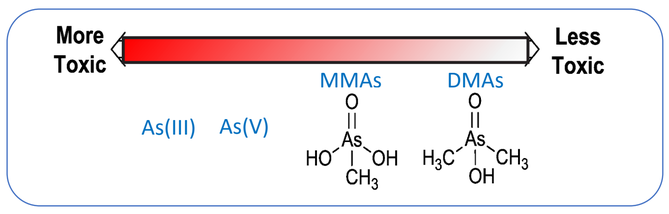
Introduction and objectives

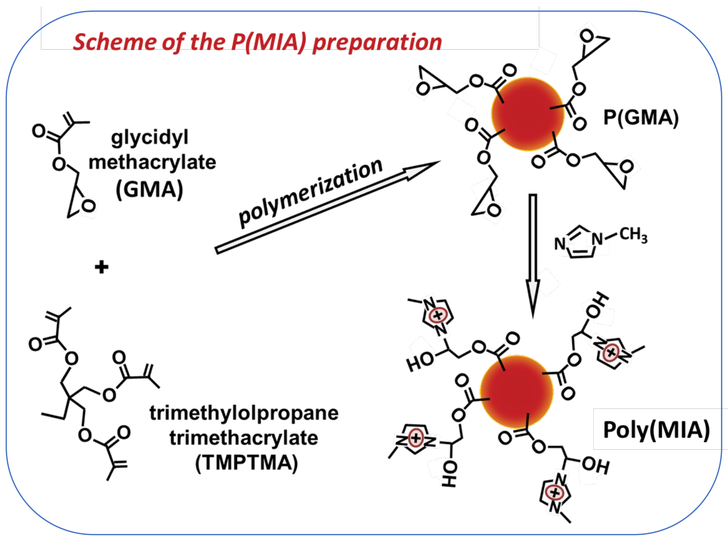
Arsenic is commonly recognized as a hazardous element. The toxicity of As depends on its chemical forms. Therefore, precise determination of low concentrations of different arsenic species in real samples is absolutely necessary to estimate the environmental impact and potential health risks. The development of fast and selective methods for the quantification of arsenic based on solid-phase extraction (SPE) with a suitable sorbent is an effective approach to control the quality of water samples. The objectives of this study are focused on synthesis of new ionic liquid-based polymer gel (called poly(MIA)) and its application for arsenic determination and speciation in surface waters.



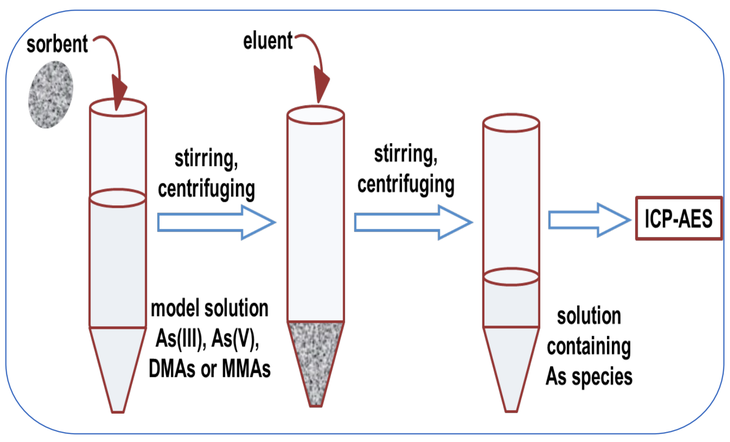
Methodology

- P(MIA) was synthesized via chemical modification of polymeric precursor with 1-methylimidazole.

Scheme of the P(MIA) preparation



- The polymer particles obtained were characterized using elemental, FTIR, SEM and BET analyses.
- The adsorption properties of poly(MIA) toward As(III), As(V), monomethylarsonic acid (MMAs) and dimethylarsinic acid (DMAs) were studied by batch procedure.



- The isotherm and kinetic models were used to elucidate the adsorption behavior of the As species.

Isotherm models

Langmuir isotherm model: $\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{b.Q_{max}}$

Freundlich isotherm model: $\ln Q_e = \ln k_F + n^{-1}.\ln C_e$

Dubinin–Radushkevich isotherm model: $\ln Q_e = \ln Q_{max} - \beta.\varepsilon^2$

$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right]$ $E_{DR} = \frac{1}{\sqrt{2\beta}}$ $R_L = \frac{1}{1+b.C_0}$

Kinetics models

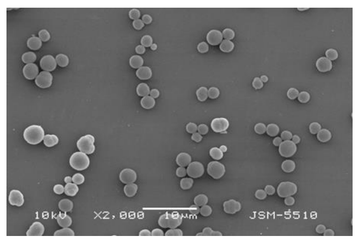
Pseudo-first-order kinetics model: $\ln Q_e = \ln k_F + n^{-1}.\ln C_e$

Pseudo-second-order kinetics model: $\frac{t}{q_t} = \frac{1}{k_1.q_e^2} + \frac{t}{q_e}$

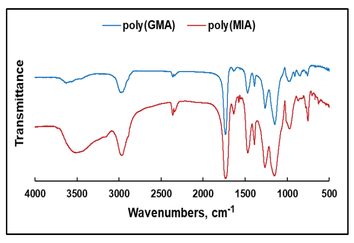
Intra-particle diffusion model: $q_t = k_{diff}.t^{1/2} + C$

Results

Characterization



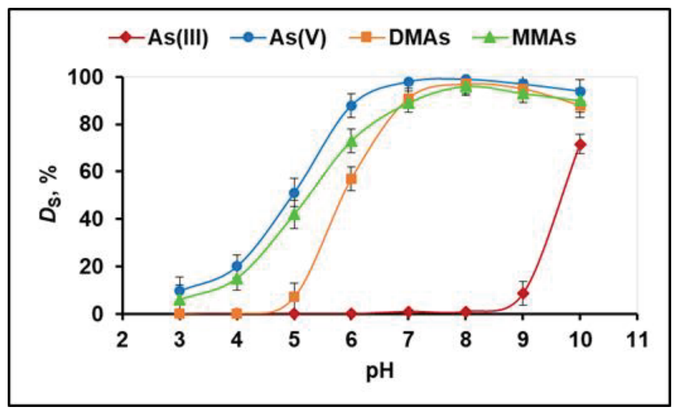
SEM image of poly(MIA)



FTIR spectra

Specific surface area: 27 m^2/g; total pore volume: 0.10 m3/g; Average pore diameter: 15 nm

Extraction efficiency of poly(MIA) toward arsenic species

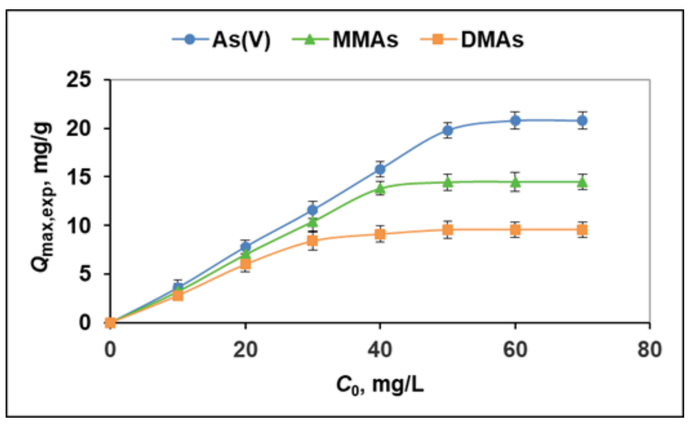


pH-dependence

Degree of elution (%) for As(V), DMAs and MMAs from poly(MIA) using different eluents

Eluent solution	D_E, %		
	As(V)	DMAs	MMAs
0.5 mol/L CH_3COOH	< 3	86±3	87±2
1.0 mol/L CH_3COOH	< 3	99±2	99±2
0.5 mol/L HCl	65±3	99±2	98±2
1.0 mol/L HCl	77±3	99±2	99±2
2.0 mol/L HCl	99±2	99±2	99±2
3.0 mol/L HCl	99±2	99±2	99±2

Adsorption isotherms



Effect of the initial concentration of As(V), DMAs and MMAs on the adsorption capacity of poly(MIA)

Experimental and fitting parameters of the various isotherm models for adsorption of As(V), DMAs and MMAs ions onto the poly(MIA) (25°C)

Adsorption isotherm model	Parameters	As(V)	DMAs	MMAs
Experimental adsorption capacity	$Q_{max,exp}$ (mg/g)	20.78	9.58	14.50
Langmuir	$Q_{max,calac}$ (mg/g)	20.53	9.64	14.45
	b (L/mg)	0.45	0.76	0.69
	R^2	0.9931	0.9981	0.9937
	R_L	0.03 – 0.10	0.02 – 0.12	0.02 – 0.13
Freundlich	k_F	6.78	8.02	6.37
	n	2.74	9.92	4.00
	R^2	0.9755	0.9505	0.9086
Dubinin-Radushkevich	$Q_{max,calc}$ (mg/g)	14.65	8.76	12.12
	β (mol²/kJ²)	0.11	0.36	0.18
	E_{DR} (kJ/mol)	2.16	1.18	1.67
	R^2	0.8355	0.9218	0.9003

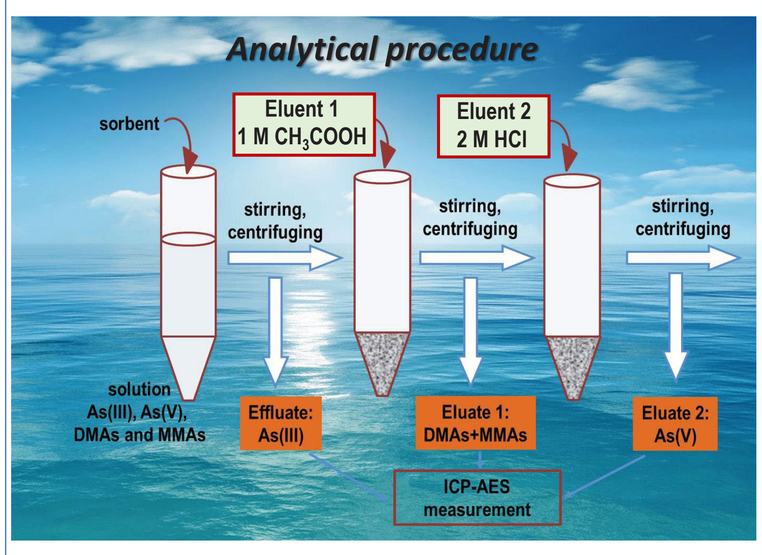
The analysis of the data presented in Table shows that the correlation coefficients obtained for Langmuir isotherm have higher values compared with the values obtained when experimental data are modeled using Freundlich and Dubinin–Radushkevich isotherm models. Therefore, the sorption process occurs as a surface monolayer on homogeneous sites.

Adsorption kinetics

Kinetics model	Parameters	As(V)	DMAs	MMAs
Experimental adsorption capacity	$q_{e,exp}$ (mg/g)	0.7936	0.7640	0.7816
Pseudo-first-order model	$q_{e,calc}$ (mg/g)	0.2988	0.3175	0.3103
	k_1 (1/min)	0.1292	0.0882	0.1135
	R^2	0.9647	0.9320	0.9629
Pseudo-second-order model	$q_{e,calc}$ (mg/g)	0.8317	0.8095	0.8244
	k_2 (g/mg·min)	0.7222	0.4479	0.5860
	R^2	0.9936	0.9994	0.9995
Intra-particle diffusion model Region 1	k_{diff} (mg/g·min$^{1/2}$)	0.0650	0.0895	0.0757
	C (mg/g)	0.4886	0.3285	0.4240
	R^2	0.9973	0.9854	0.9990
Intra-particle diffusion model Region 2	k_{diff} (mg/g·min$^{1/2}$)	0.0086	0.0154	0.0094
	C (mg/g)	0.7395	0.6556	0.7191
	R^2	0.8304	0.7701	0.9451

The results prove that the rate limiting step is the chemisorption of As(V), DMAs and MMAs ions onto polymer gel, thus confirming strong interactions of methylimidazolium fragments in poly(MIA) with studied ions.

Analytical Application



Added/Found method applied for water samples (three parallel determinations)

	Added, µg/L			Found, µg/L		
	As(V)	As(III)	(DMAs+MMAs)	As(V)	As(III)	(DMAs+MMAs)
Lake Ognyanovo	1.0	-	0.1	1.1±0.1	<DL	0.09±0.01
	5.0	1.0	0.2	4.9±0.2	1.2±0.1	0.18±0.02
	0.5	0.2	0.1	0.4±0.1	0.18±0.02	0.11±0.02
River Iskar	1.0	-	0.1	0.9±0.1	<DL	0.12±0.02
	5.0	1.0	0.2	4.8±0.2	1.1±0.1	0.19±0.02
	0.5	0.2	0.1	0.5±0.1	0.21±0.02	0.09±0.02
Black sea water	2.0	0.1	0.05	1.9±0.2	0.11±0.01	0.044±0.003
	4.0	0.2	0.05	3.9±0.3	0.19±0.02	0.052±0.003
	10.0	0.5	0.1	10.1±0.9	0.51±0.03	0.09±0.01

Analytical characteristics of the proposed method.

Determination limit, µg/L			Relative standard deviation, % Concentration range 0.01-20 µg/L		
As(V)	As(III)	(DMAs+ MMAs)	As(V)	As(III)	(DMAs+ MMAs)
0.001	0.01	0.001	4-10	5-8	5-10

Conclusion

A non-chromatographic analytical procedure is developed for arsenic speciation in different types of surface waters. The separation of As(III), As(V), MMAs+DMAs is achieved by selective sorption/elution on/from the surface of the newly synthesized ionic liquid modified polymeric gel (poly(MIA)). The sorbent composition and structure are characterized by elemental analysis, FTIR, SEM, and nitrogen adsorption–desorption measurements. Experimental results and calculated adsorption capacities Q_{max} revealed the adsorption of As(V), DMAs and MMAs ions on homogeneous sites on the surface of the sorbent in a monomolecular layer. Kinetic studies prove that the rate limiting step is the chemisorption (ion exchange) of As(V), DMAs and MMAs ions onto the polymer gel surface.

The poly(MIA)was used as a solid phase for arsenic speciation in water samples. The advantages of the proposed analytical procedure are: (i) no need to use additional chelate complex forming reagent (ii) no need to use reagents for pre-oxidation or pre-reduction of the arsenic species; (iii) all analytical steps might be performed in one analytical vessel (centrifugation tube); (iv) determination limits achieved ensured successful application for arsenic content assessment in monitoring campaign.

The developed analytical method was validated by the analysis of certified refer-ence material in this way confirming the accuracy of the results obtained.

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