Journal of the Serbian Chemical Society
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J. Serb. Chem. Soc. 90 (5) S212-S215 (2025)
Supplementary material

SUPPLEMENTARY MATERIAL TO

Amino-starch derivates for adsorption of specific pharmaceuticals and pesticides in contaminated water: Examination in both spiked and real water samples

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J. Serb. Chem. Soc. 90 (5) (2025) 693–707

EXPERIMENTAL

Materials and chemicals

The following materials and chemicals were used to prepare the starch samples: potato starch (loss on drying at 105 °C < 10%, sulfured ash < 0.5%, SuperLab, Serbia), melamine (2,4,6-triamino-1,3,5-triazine, 99%, Thermo Fisher), L(–)-cysteine ((R)-2-amino-3-mercaptopropionic acid, ≥ 97%, Thermo Fisher), L-histidine ((S)-2-amino-3-(4-imidazolyl)propionic acid, ≥ 98.5%, Carl Roth), bentonite clay (nanoclay, Sigma-Aldrich) and diatomaceous earth (SiO_2 95%, Sigma-Aldrich).

Pharmaceuticals and pesticides selected for the study were the most commonly used and frequently detected in the investigated area (Table 1). High purity (> 95%) analytical standards of four chosen pharmaceuticals: erythromycin, lorazepam, diazepam and clopidogrel were provided by national pharmaceutical companies (Hemofarm, STADA Group, Vršac, Serbia and Zorka-Pharma, Šabac, Serbia). The analytical standards of four selected pesticides: atrazine, propazine, malathion and tebufenozide were supplied from Riedel-de Haën (Seelze, Germany).

The stock standard solutions were prepared in methanol at the concentration of 100 μg mL^{-1}. The working standard solutions were prepared by mixing the appropriate amounts of the stock standard solutions and diluting them with methanol. All solutions were preserved at -4 °C. All solvents used were HPLC grade from J.T. Baker (Center Valley, US) or Sigma-Aldrich (St. Louis, US) and all reagents were of analytical grade. Deionized water was obtained by passing the distilled water through a GenPure ultrapure water system (TKA, Niederelbert, Germany).

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TABLE S-I. Labels of samples

Modification		Biocomposite abbreviation
Native starch	+ Melamine	= SM
	+ Cysteine	= SC
	+ Histidine	= SH
	+ Clay (bentonite)	= S-clay
	+ Diatomaceous earth	= S-d.e
Starch-Melamine (SM)	+ Clay (bentonite)	= SM-clay
	+ Diatomaceous earth	= SM-d.e
Starch-Cysteine (SC)	+ Clay (bentonite)	= SC–clay
	+ Diatomaceous earth	= SC-d.e
Starch-Histidine (SH)	+ Clay (bentonite)	= SH-clay
	+ Diatomaceous earth	= SH-d.e

Characterization methods

Fourier-transform infrared spectroscopy (FTIR) was performed using a Nicolet iS10 spectrometer (Thermo Scientific) in the attenuated total reflectance (ATR) mode with a single bounce 45 °F Golden Gate ATR accessory with a diamond crystal and DTGS detector. FTIR spectra were obtained at 4 cm^{-1} resolution with ATR correction. The FTIR spectrometer was equipped with OMNIC software and the spectra were recorded in the wavelength range from 2.5 μm to 20 μm (*i.e.*, 4000-500 cm^{-1}).

The morphology of samples was examined using a scanning electron microscope (SEM) (type of instrument – FE-SEM, TESCAN Mira3 XMU) operating at 10 kV. Before analysis, samples were coated with gold to reduce the charging effect and improve the image quality.

X-ray diffraction (XRD) was performed using an Ultima IV Rigaku diffractometer, equipped with CuKα1,2 radiations, using a generator voltage (40.0 kV) and a generator current (40.0 mA). The range of 5–40° 2θ was used for all powders in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 2° min^{-1}, using D/TeX Ultra high-speed detector. A monocrystalline silicon sample carrier for sample preparation was used.

Adsorption performance and regeneration studies

The separation of pesticides and pharmaceuticals was conducted using a Dionex UltiMate 3000® LC system (Thermo Scientific, USA). For detection and quantification of pesticides and pharmaceuticals, LTQ XL (Thermo Scientific, USA) mass spectrometer was used with an electrospray ion source and linear ion trap mass analyzer. The gradient of the mobile phase consisting of methanol (A), water (B) and 10% acetic acid (C) is shown in Table S-I. Selected reaction monitoring (SRM) chromatograms of investigated pharmaceuticals and pesticides are given in Fig. S-1 and LC/MS-MS quantification parameters are presented in Table S-II.

TABLE S-II. Gradient and flow rate of the mobile phase

Time (min)	Flow rate ($cm^3 min^{-1}$)	Content, %		
		A	B	C
0	0.5	49	50	1
0	0.5	49	50	1
15.00	1	0	100	0
18.00	1	0	100	0
18.01	0.5	49	50	1
23.00	0.5	49	50	1

TABLE S-III. LC/MS and MS^n optimized parameters for identification of the selected pharmaceuticals and pesticides

Pollutant	Retention time, min	*m/z* Precursor ion	Collision energy a. u.*	*m/z* Product ion
Erythromycin	4.72	734.1	28	576.1
Lorazepam	6.49	321.0	32	302.9
Diazepam	8.23	285.2	40	257.2
Clopidogrel	10.72	321.9	28	211.8
Atrazine	6.50	216.0	38	174.0
Propazine	7.91	230.0	36	188.0
Malathion	8.62	331.0	28	284.7
Tebufenozide	10.01	375.0	34	225.0

* arbitrary units defined by LCQ system

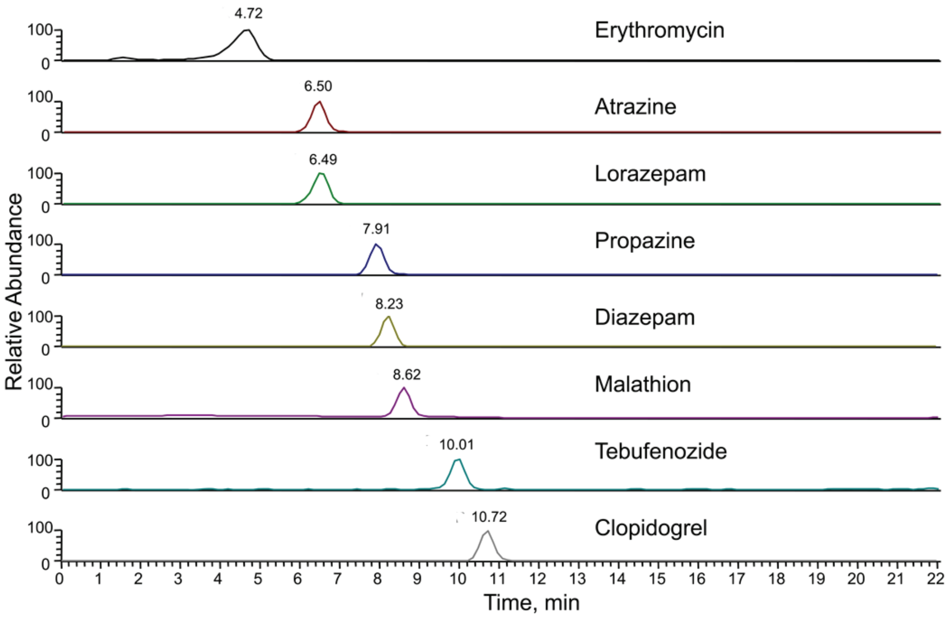

Fig. S-1. SRM chromatograms of the selected pharmaceuticals and pesticides

TABLE S-IV. Adsorption efficiency of tested materials for the removal of selected pharmaceuticals and pesticides

	Pollutant							
	Erytrom.	Atraz.	Loraz.	Propaz.	Diazep.	Malath.	Tebuf.	Chlop.
Sample	Adsorption efficiency, %							
S	33.44	12.64	21.34	19.71	17.86	18.73	19.15	19.07
SM	87.5	29.39	41.32	39.41	63.21	39.46	35.47	39.62
SC	100	30.93	51.64	50.27	68.51	61.75	77.52	78.62
SH	100	33.36	51.44	58.39	70.92	69.51	87.06	82.56
Clay	32.12	14.53	16.78	17.89	24.66	28.97	32.85	35.46
S-clay	59.6	22.77	26.69	34.65	34.49	51.45	46.66	49.11
SM-clay	94	28.72	35.72	36.9	52.57	65.45	70.66	75.67
SC-clay	100	30.05	43.67	43.75	53.19	78.58	80.54	82.57
SH-clay	100	32.58	50.78	44.91	55.97	81.53	82.54	86.86
d.e	35.58	14.76	22.72	22.21	25.37	27.85	24.62	26.29
S-d.e	83	29.79	34.45	29.27	28.27	38.49	47.44	44.19
SM-d.e	94.82	38.38	37.22	40.27	41.99	56.7	66.69	71.51
SC-d.e	98	44.02	39.33	39.74	41.6	59.03	72.75	75.97
SH-d.e	98.21	45.04	41.41	28.39	45.24	62.89	79.49	86.03

TABLE S-V. Adsorption efficiency of tested materials for the removal of selected pharmaceuticals and pesticides from real water samples

	Pollutant							
	Erytrom.	Atraz.	Loraz.	Propaz.	Diazep.	Malath.	Tebuf.	Chlop.
Sample	Adsorption efficiency, % (distilled water)							
SM	87.5	29.39	41.32	39.41	63.21	39.46	35.47	39.62
SC	100	30.93	51.64	50.27	68.51	61.75	77.52	78.62
SH	100	33.36	51.45	58.39	70.92	69.51	87.07	82.56
Adsorption efficiency, % (surface water)								
SM	96.94	12.39	21.83	19.45	63.18	91.28	80.19	92.53
SC	92.29	14.48	30.04	16.34	70.76	89.88	77.09	90.52
SH	69.22	32.59	29.68	32.62	32.89	76.67	83.33	82.18
Adsorption efficiency, % (groundwater)								
SM	96.13	14.62	18.28	18.4	77.11	95.29	81.75	88.08
SC	91.26	18.39	32.87	22.05	76.06	84.92	74.99	83.99
SH	64.31	31.98	24.55	32.31	22.45	83.71	82.2	82.11
Adsorption efficiency, % (wastewater)								
SM	98.7	48.05	62.19	69.99	79.57	96.6	90.86	95.15
SC	94.05	57.98	72.31	25.91	73.65	91.59	89.79	92.49
SH	53.78	38.93	42.08	28.97	44.84	85.51	89.46	88.44