



ACCEPTED MANUSCRIPT

This is an early electronic version of an as-received manuscript that has been accepted for publication in the Journal of the Serbian Chemical Society but has not yet been subjected to the editing process and publishing procedure applied by the JSCS Editorial Office.

Please cite this article as N. Palić, M. Vukčević, M. Maletić, M. Mirković, M. Ristić, A. Perić Grujić and K. Trivunac, *J. Serb. Chem. Soc.* (2025) <https://doi.org/10.2298/JSC240919007P>

This “raw” version of the manuscript is being provided to the authors and readers for their technical service. It must be stressed that the manuscript still has to be subjected to copyediting, typesetting, English grammar and syntax corrections, professional editing and authors’ review of the galley proof before it is published in its final form. Please note that during these publishing processes, many errors may emerge which could affect the final content of the manuscript and all legal disclaimers applied according to the policies of the Journal.



J. Serb. Chem. Soc. **00(0)** 1-15 (2025)
JSCS-13054

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

NATAŠA PALIĆ^{1*}, MARIJA VUKČEVIĆ², MARINA MALETIĆ¹, MILJANA MIRKOVIĆ³,
MIRJANA RISTIĆ², ALEKSANDRA PERIĆ GRUJIĆ² AND KATARINA TRIVUNAC²

¹Innovation Center of Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia, ²University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia, and ³University of Belgrade, Vinča Institute of Nuclear Sciences – National Institute of the Republic of Serbia, 12–14 Mike Petrovića Alasa Street, Vinča, 11000 Belgrade, Serbia.

(Received 19 September 2024; revised 3 December 2024; accepted 10 January 2025)

Abstract: In this study, the possibility of using modified potato starch, with nitrogen-containing chemical agents (melamine, cysteine, and histidine) as green adsorbents for removing pharmaceuticals and pesticides from water has been investigated. The influence of additional modification of amino-starch with clay and diatomaceous earth was examined. The effect of the applied modification on the structural, surface, and morphological properties was determined by FTIR, XRD, and SEM analysis, while the adsorption properties were determined through the effectiveness of prepared materials to remove selected pollutants from spiked and real water samples. The efficiency of investigated amino-starches for the adsorption of pharmaceuticals and pesticides decreases in order: starch-histidine > starch-cysteine > starch-melamine, with a slightly better efficiency for pharmaceuticals adsorption. Additional modification of amino-starches with clay/diatomaceous earth did not contribute to the increase in adsorption efficiency. It was found that the influence of the matrix of real water samples on the adsorption efficiency is up to 10 %, which represents a promising potential for applying amino-starch as a cheap and effective adsorbent for wastewater treatment. Also, starch-histidine and starch-cysteine showed the possibility of reusing up to three cycles of adsorption.

Keywords: potato starch; modification; adsorption; organic pollutants; reuse.

INTRODUCTION

Growing world population, increased investment in medical research, innovations in the field of medicine, ubiquitous availability of the global market,

* Corresponding author. E-mail: nkaric@tmf.bg.ac.rs
<https://doi.org/10.2298/JSC240919007P>

increase in chronic diseases, as well as the prevention and treatment of animal diseases in intensive livestock have led to a significant increase in the consumption of pharmaceuticals in the last few decades.^{1,2} Exposure of non-target organisms to even low concentrations of pharmaceutical products can have negative effects reflected in ecotoxicity (acute and chronic toxicity, genotoxicity, and carcinogenicity); pharmacological effects (hormone and immune system interference), and the development of microorganism resistance.³ Another category of pollutants frequently identified in water is pesticides. About 85 % of the world's pesticide production is spent on agricultural purposes, crop protection, and chemical control of various pests, such as insects, bacteria, fungi, and algae in electrical equipment, refrigerators, paints, paper, cardboard, and food packaging materials. Adverse effects on human health have been observed even at very low concentrations of pesticides. Pesticide poisoning can lead to various diseases, such as cancer, hormonal disorders, asthma, various allergies, birth defects, and fetal death.⁴

In the field of environmental engineering, adsorption plays an integral role among methods to treat wastewater because of its robustness in handling a range of pollutants, simplicity in operation, low operating costs, simplicity of the process, and variety of materials that can be used as adsorbents.⁵ Natural material, starch, is an attractive material for adsorption application, due to its low cost, availability in nature in large amounts, biorenewability, non-toxicity, and good adsorption characteristics. Previous studies have shown that chemical modification, i.e., the inclusion of functional groups in the backbone of starch, improves the efficiency of modified starch for the adsorption of various organic and inorganic pollutants from water.^{5,6}

Following the goals of sustainable development, this research brings a novel approach to the modification of natural materials and the preparation of a green adsorbent that can be used for wastewater treatment. The chemical modification of starch with melamine and amino acids was carried out to increase the number of active sites for adsorption, while the physico-chemical modification with clay/diatomaceous earth was carried out to increase the stability of starch in the aqueous environment. It is also expected that modification with clay and diatomaceous earth will increase adsorption efficiency, due to their good adsorption properties.

In this work, the adsorption of selected pharmaceuticals (erythromycin, lorazepam, diazepam, and clopidogrel) and pesticides (atrazine, propazine, malathion, and tebufenozide) from spiked water and real water samples (surface water, groundwater, and wastewater) was examined. Chemically modified starch with nitrogen-rich compounds (melamine, cysteine, histidine) and materials based on amino-starch derivatives additionally modified by adding bentonite clay and diatomaceous earth were used as adsorption materials. The applied adsorption

process using modified starch can be considered ecologically sustainable and economically acceptable, due to the use of natural materials modified by a simple and safe method, solving the extremely important problem concerning the presence of pharmaceutical products and pesticides in the environment. In order to assess the cost-effectiveness and sustainability of the application of amino-starch derivatives as adsorbents for the removal of selected pharmaceuticals and pesticides in real systems, their reuse was examined.

EXPERIMENTAL

Materials and chemicals

Details of materials and chemicals are given in the Supplementary material.

Preparation of amino-modified starch

Amino-modified starch (AMS) was synthesized according to our previous reports.⁵ The synthesis of the material with melamine was carried out at a temperature of 80 °C until the melamine was dissolved in the presence of acetic acid and distilled water. After the addition of oxidized starch, the reaction was conducted at 30 °C for another 2 h with stirring at 400 rpm. After washing and filtering, the obtained material was dried at 50–60 °C to a constant mass. Modification with cysteine and histidine was performed by mixing oxidized starch with distilled water for 30 min at 40 °C to obtain a starch suspension to which the amino acid was then added and stirring at 400 rpm was continued at 40 °C for another 3 h. The resulting mixture was filtered and washed several times and then dried at 50 °C to constant weight.

Preparation of biocomposites

The preparation of starch-based biocomposites was carried out according to methods described in the literature with some changes.^{7,8} AMS (5 g) was suspended in 30 mL of deionized water and kept in a water bath at 70 °C with continuous stirring at 400 rpm for 1 h. The clay/diatomaceous earth (0.5 g) was dispersed in 30 mL of deionized water and the dispersion was poured into the gelatinized starch/AMS solution. The reaction was continued at 60 °C with constant stirring on a magnetic stirrer at 400 rpm for 3 h. The sample was dried at 50 °C in an oven, and finally, the dry sample was ground into a powder. Samples with native starch and clay/diatomaceous earth were prepared in the same way. Obtained starch-based biocomposites were labeled according to Table S-I.

Characterization methods

The determination of the surface, structural, and morphological characteristics of the material was carried out using Fourier-transform infrared spectroscopy (FTIR), a scanning electron microscope (SEM), and X-ray diffraction (XRD). Details of these characterization methods are given in the Supplementary material.

Adsorption performance and regeneration studies

The adsorption efficiency of examined samples was investigated in a batch system with constant mixing (180 rpm) at room temperature. The adsorption of selected pharmaceuticals (erythromycin, lorazepam, diazepam, and clopidogrel) and pesticides (atrazine, propazine, malathion, tebufenozide) from multi-component spiked water samples, surface water, groundwater, and wastewaters was investigated. Adsorption tests were performed at constant adsorbent dosage (0.05 g), initial concentration (500 mg dm⁻³), and solution volume (10 mL) for 180 min, in the batch system with constant shaking at room temperature. The initial pH of

the pesticides/pharmaceuticals solution and adsorbent was about 5, for all samples. After adsorption, all samples were filtered through the PVDF 0.45 µm filters.

The adsorption efficiency (%) of selected pharmaceuticals and pesticides from aqueous solutions was calculated according to the equation:

$$\text{Adsorption efficiency, \%} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

where C_0 and C_t (mg dm^{-3}) are the concentrations of a pollutant at the initial time and after time t (min).⁵

For regeneration investigation, the dried adsorbents were immersed in 0.05 mol/L HNO_3 solution for 120 minutes with constant stirring at room temperature. After that, adsorbents were washed with deionized water and dried at 50 °C for the next adsorption cycle.

The concentration of selected pesticides and pharmaceuticals was analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Details related to this instrumental technique are given in the Supplementary Material.

RESULTS AND DISCUSSION

FTIR analysis

FTIR spectra of all examined samples are presented in Fig. 1. The spectra of all modified starch/AMS samples exhibit a broad absorption band at approximately 3330 and 3335 cm^{-1} , which can be attributed to the stretching vibration of O–H groups from the glucose unit. A small peak at 2993, 2930, and 2928 cm^{-1} , present in FTIR spectra of all tested samples, can be assigned to symmetrical and asymmetric C–H vibrations in methyl or methylene groups. An intense absorption band at 1001 and 1004 cm^{-1} is typical in the spectra of starch and its derivative and attributed to the $\text{CH}_2\text{--O--CH}_2$ stretching vibrations of anhydroglucose unit.⁹ The weaker absorption peak at 1710, 1720, and 1725 cm^{-1} in the spectra of the modified AMS samples can be attributed to --C=O stretching vibrations.¹⁰ The absorption peak at 3121, 3124, and 3127 cm^{-1} in the FTIR spectrum of SM-clay, SM-d.e, and SM is assigned to --NH_2 stretching vibration; whereas those at 1542, 1540, 808, and 764 cm^{-1} are assigned to the triazine ring.¹¹ In the FTIR spectrum of SC, SC-clay, and SC-d.e, the absorption peak at 1583, 1580 and 1565 cm^{-1} can be attributed to the presence of the --C=N group, while the peak at 2553, 2530, and 2536 cm^{-1} corresponds to the S–H stretching vibrations.¹² In the FTIR spectrum of SH, SH-clay, and SH-d.e, the peak at 1483 and 1480 cm^{-1} corresponds to the bending vibration of the --NH_2 group, while the ring vibration appears at 635, 630, and 623 cm^{-1} .¹² The characteristic peaks for bentonite clay corresponding to the Si–O and Al–O vibrations (3691, 3620, 832 and 693 cm^{-1})¹³ can be seen in Fig. 1c. The absorption bands corresponding to Si–O, O–Si–O and Si–O–Si vibrations in the diatomaceous earth structure are observed at 1076, 812 and 703 cm^{-1} (Fig. 1d).^{13,14}

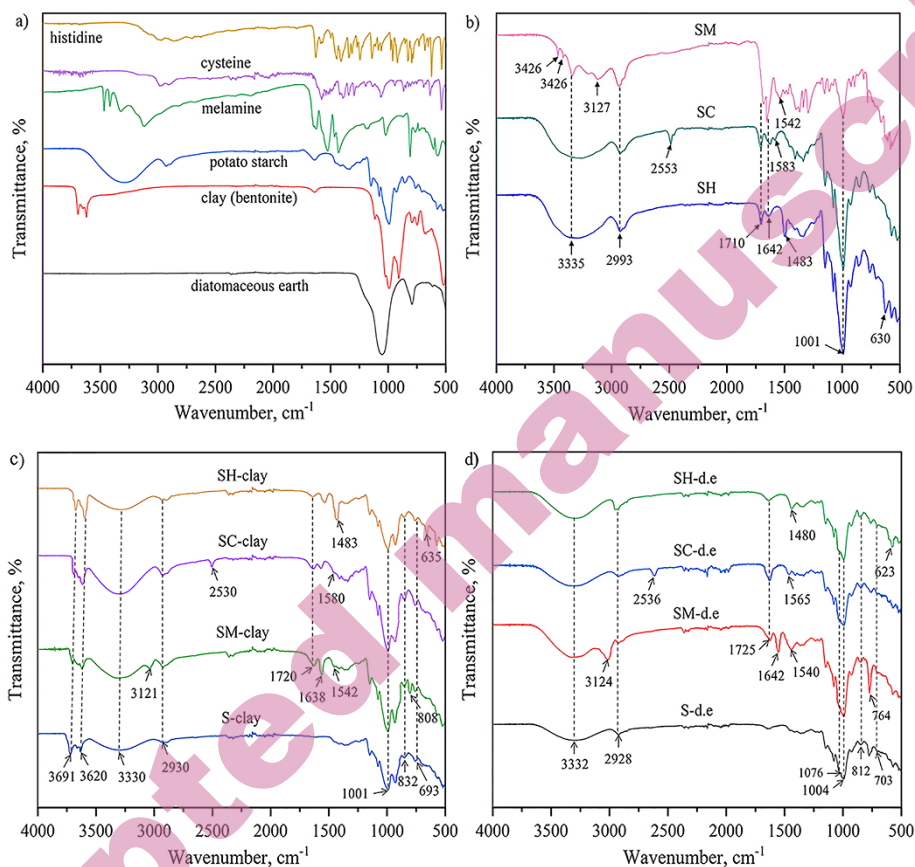


Fig. 1. FTIR spectra of examined starch-based adsorbents

SEM analysis

Fig. 2 shows SEM micrographs of all tested samples. The micrographs of bentonite clay (Fig. 2a) indicate the existence of a roughed matrix, i.e. a crystalline morphology with the dominance of platelet shapes in the section and a certain degree of porosity.¹⁵ Fig. 2b shows the smooth surface of natural potato starch granules, typically elliptical and spherical shapes without any cavities or cracks. SEM micrographs of diatomaceous earth (Fig. 2c) show the presence of a porous structure in the form of a honeycomb with impurities that can be incorporated into the new material during modification.¹⁶

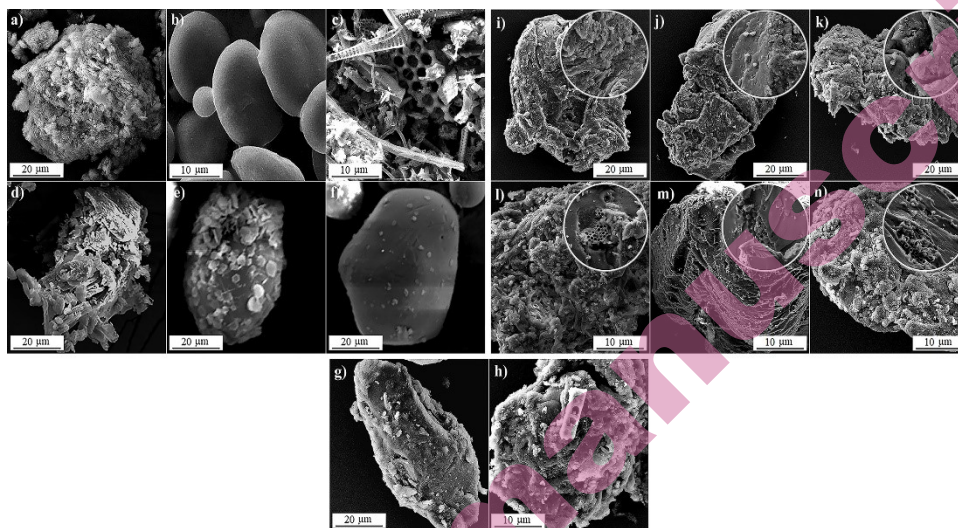


Fig. 2. SEM micrographs of clay (bentonite) (a); potato starch (b); diatomaceous earth (c); SM (d); SC (e); SH (f); S-clay (g); S-d.e. (h); SM-clay (i); SC-clay (j); SH-clay (k); SM-d.e (l); SC-d.e (m); and SH-d.e (n)

Fig. 2d-f show SEM micrographs of amino-modified starches, with melamine, cysteine, and histidine, respectively. Since there was no harsh physical treatment or application of high temperatures during the modification process, the starch granules retained their original shape. The success of modification was confirmed by the surface roughness, i.e. the presence of unevenness and impurities in the structure of the new materials originating from amino derivatives. Fig. 2d shows the presence of melamine as crystalline segments, not only on the surface of the starch granules but even within the inner parts of the starch granules. In the case of starch modified with cysteine (Fig. 2e), the presence of cysteine is observed on the surface of the starch, in the form of stuck parts, while in the case of starch modified with histidine, a more homogeneous structure is observed, i.e. fewer parts on the surface, which means that histidine coats the starch granules to a greater extent, and less sticks to the surface (Fig. 2d). In the second part of the modification, the possibility of reacting starch/amino-modified starch with clay/diatomaceous earth was examined. The reaction is simply carried out by adding clay, or diatomaceous earth, to a gelatinized starch solution or amino-modified starch. All SEM micrographs (Fig. 2g-2n) clearly show that the form of starch granules has been changed, but that the shape is not completely destroyed. The edges have lost clear boundaries, the surface has become rough, with protrusions and cracks, while in

the cross-section of the starch granules, parts originating from the initial components, amino derivatives, clay, and diatomaceous earth can be observed.

XRD analysis

Comparative XRD diagrams for investigated samples are presented in Fig. 3. Native potato starch showed the typical B-type X-ray pattern with reflection diffraction peaks (2θ) at 5.3, 15.1, 17.5, 19.5, 22.5, 24.1, and 26.4°. The characteristic XRD peaks for bentonite clay (Fig. 3b) at the diffraction angle, $2\theta = 12.5, 20.8^\circ, 26.5^\circ, 35.3^\circ, 36.7^\circ, 38.9^\circ,$ and 55.2° can be associated with the presence of the smectite and impurities such as opal, quartz, and calcite in the structure of pure bentonite clay. The XRD pattern of diatomaceous earth (Fig. 3c) revealed the main phase of non-crystalline opal-A with the characteristic broad peak centered at 21.3° .

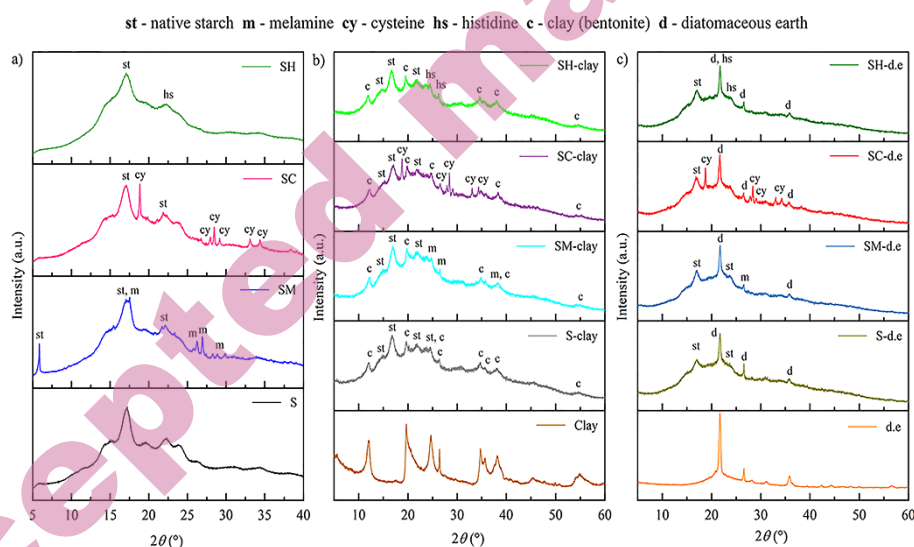


Fig. 3. XRD patterns of examined starch-based adsorbents

Compared to native starch (Fig. 3a), additional peaks for SM appearing at $2\theta = 5.92^\circ, 17.5^\circ, 22.7^\circ$ and ranging from 25.5° to 30.2° originate from melamine, while the peaks for SC that are characteristic of the cysteine structure were observed at $2\theta = 18.8^\circ$ and in the range from 27.8° to 34.4° . A significant decrease in crystalline domains was observed for SH, where a decrease in peak intensity is observed in the interval from 19.6° to 24.1° compared to native starch, while the characteristic peaks for the structure of pure histidine, ranging from 16.2° to 28.3° were not visible, as a consequence of their lower intensity and overlap with the characteristic peak of the starch structure. Figs. 3b and 3c show that, in addition to the characteristic XRD peaks originating from the structure of starch and amino

derivates, XRD peaks characteristic for bentonite clay (Fig. 3b), and diatomaceous earth (Fig. 3c) are also present.²³ Based on the XRD patterns of the tested samples, it can be concluded that the additional modification of the samples with bentonite clay (Fig. 3b) and diatomaceous earth (Fig. 3c) contributes to the increase of crystalline domains in the materials compared to the native starch and amino-modified samples (Fig. 3a).

Adsorption study

The adsorption efficiency values of examined materials to adsorb selected pharmaceuticals and pesticides from spiked deionized water are presented in Fig. 4 and Table S-IV. It can be noticed that the modification of starch contributed to an increase in the efficiency of pharmaceutical and pesticide adsorption two to three times compared to adsorption on unmodified starch. Applied modifications significantly contributed to the adsorption efficiency, and the modification of starch with amino acids, especially histidine, contributed the most to the high percentage of all selected pollutants adsorption. Also, the same adsorption trend for pharmaceuticals (erythromycin > clopidogrel > diazepam > lorazepam) and pesticides (tebufenozide > malathion > propazine > atrazine) has been observed for all examined materials. The order of the affinity obtained can be explained by the different intensities of electrostatic forces acting between the positively charged surface of all amino-modified starch samples, on one hand, and molecules of pharmaceuticals and pesticides, on the other. All tested materials showed a slightly better efficiency for the removal of pharmaceuticals, than for pesticides. The order of the adsorption efficiency for clopidogrel > diazepam > lorazepam indicates that the adsorption efficiency decreases with increased polarity of the pharmaceutical (SRM chromatograms, Fig. S-1). The exception is erythromycin, possibly as a consequence of its large molecular mass, as well as of the highest electronegativity of this molecule compared to other pollutants. This could also explain, why the erythromycin molecules bind to the surface of the adsorbent first, and then the molecules of other pollutants. The same explanation applies to the adsorption efficiency of pesticides; with increasing polarity of pesticide molecules (SRM chromatograms, Fig. S-1) the adsorption efficiency decreases (tebufenozide > malathion > propazine > atrazine). Based on all of the above, it can be stated that the investigated materials are more suitable for the adsorption of less polar compounds.

Additional modification of starch with clay and diatomaceous earth had no significant influence on the adsorption properties of amino materials. As a result of the starch surface modification with clay and diatomaceous earth (Fig. 2), the surface of the starch granules was coated with parts of clay/diatomaceous earth, which reduced its porosity and the number of available sites for adsorption.

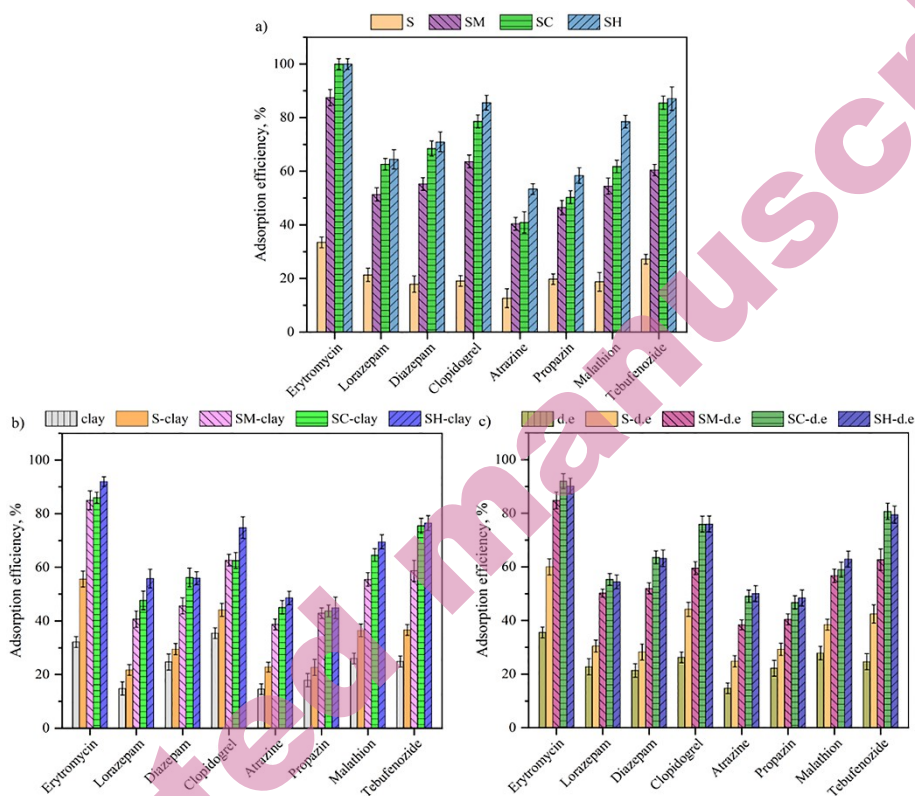


Fig. 4. Adsorption efficiency of examined starch-based adsorbents

Adsorption study in real water samples

Following the results obtained in the previous part, amino-starch samples modified with melamine and amino acids were selected for testing the adsorption of pharmaceuticals and pesticides from spiked real waters. Three samples of real water, a sample of surface water collected from river Pek, Serbia; a sample of groundwater, collected from Belgrade Ranney wells, Serbia; and a sample of wastewater from the entrance to the water purification plant Arandelovac, Serbia; were analyzed (Fig. 5, Table S-V). The results obtained for spiked deionized water were compared to the results for real water samples to examine the matrix effect, i.e., the influence of components present in water matrix on the adsorption efficiency of used adsorbents. One of the most important factors that can affect the efficiency of adsorption is the presence of dissolved organic matter (DOM), which consists of different size fractions (i.e. building blocks, humic and fulvic acids, biopolymers, and low molecular weight organic matter) that can interfere with the adsorption process by blocking the pores of the adsorbent or competing with the contaminants of interest for adsorption sites.²⁴ According to the literature, the

effect of adsorbent saturation is more pronounced when dealing with the adsorption of anionic compounds because DOM is negatively charged at the overall pH of the wastewater and interferes with the adsorption of anionic compounds through electrostatic repulsion.²⁵ However, many studies show that DOM does not have a significant effect or can even have a positive effect on the adsorption of some organic products, depending on the experimental conditions, which has also been confirmed in this research.^{26,27}

Changes in adsorption efficiencies of up to 10 % were observed compared to the adsorption from deionized water. A particularly significant result was the increase in the removal efficiency of almost all pharmaceuticals and pesticides from wastewater suggesting that the matrix of real water samples either has no significant influence or has a positive influence on the adsorption efficiency.

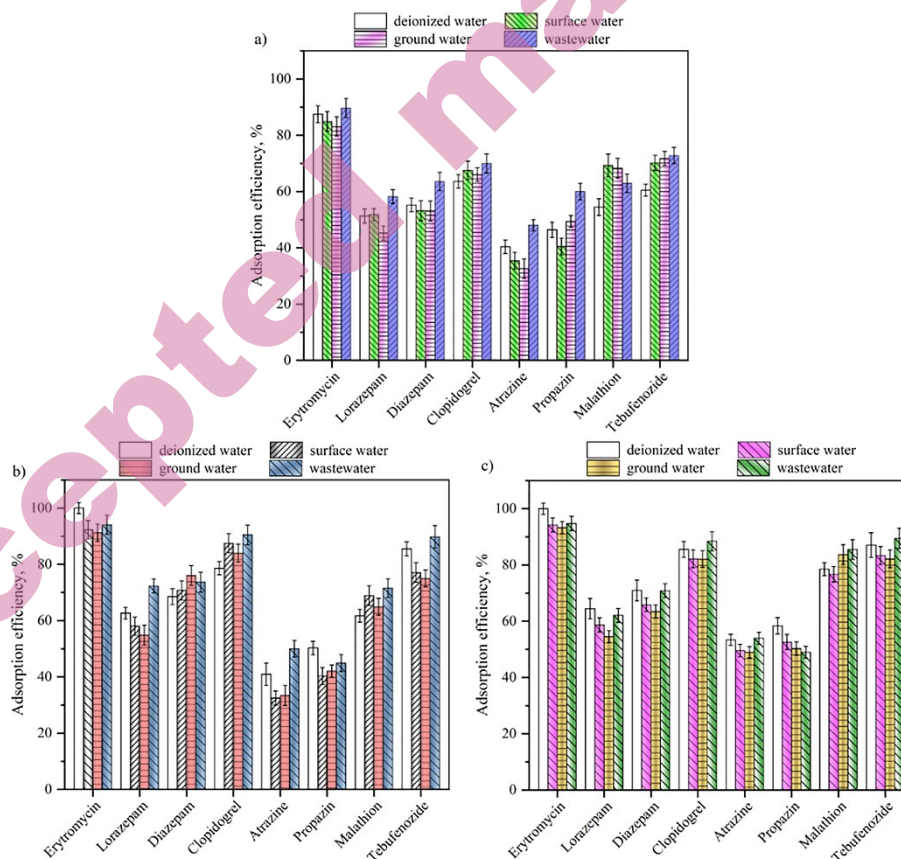


Fig. 5. Adsorption efficiency of amino-modified starches, SM (a), SC (b), and SH (c) for the removal of selected pharmaceuticals and pesticides from real water samples

Comparative study of different adsorbents – literature review

Table I shows data from the literature on the use of different types of modified starch for the removal of different pharmaceuticals and pesticides from water. By comparing the adsorption efficiency, the modified starch obtained in this study gives comparable results with literature data, bearing in mind that it is a different type of starch modification, type of pollutant, and different experimental conditions that significantly affect the adsorption efficiency. Also, it is important to point out that the adsorption of selected pharmaceuticals and pesticides in this work was performed from a mixture of several pharmaceuticals and pesticides, which helps to evaluate the efficiency of these adsorbents for application in the treatment of real wastewater because wastewater often contains more than one pollutant.

In most of the studies from Table I for obtaining starch-based adsorbents for the removal of pharmaceuticals and pesticides, complex procedures lasting several hours, at high temperatures, with the use of expensive and toxic chemicals were used.^{28, 29, 30, 31} The main advantage of the amino starch derivatives obtained in this work is the method of their obtaining, which is based on a simple and quick procedure, without the use of expensive and toxic solvents, without by-products, with minimal consumption of electricity, and the use of starch modifiers that are environmentally acceptable and safe for use (amino acids and melamine), which is in accordance with the principles of green chemistry and sustainable development.

Regeneration and reuse study

The results of the reuse of amino-starch derivatives synthesized in this study are shown in Fig. 6. Desorption and reuse were investigated for the two adsorbents that showed the highest adsorption efficiency for all tested pollutants, that is starch modified with cysteine (Fig. 6a) and starch modified with histidine (Fig. 6b). The adsorption efficiency of the tested adsorbents decreases significantly, by 12-15 %, after the first cycle. The reason for this may be the disruption of the functional structure due to treatment with a desorption agent, i.e. nitric acid.²⁹ After the second cycle, the efficiency decrease is smaller than the first, so three adsorption cycles are optimal for both investigated adsorbents.

TABLE I. Modified starches for the adsorption of different pharmaceuticals and pesticides

Adsorbent	Type of pollutant	Adsorption efficiency	Ref.
<i>Pharmaceuticals</i>			
Starch/porous carbon	Tetracycline	67.16 %	28
Grafted starch with octenyl succinic anhydride	Cephalexin	0.92 mg g ⁻¹	32
Starch-g-P(AM-co-AMPS)	Tetracycline	95.7 %	33
Crosslinked starch/chitosan	Tetracycline	99.4 %	34
	Ciprofloxacin		
Carboxymethyl starch-modified magnetic bentonite clay	Tetracycline	169.7 mg g ⁻¹	29
<i>Pesticides</i>			
Starch/porous carbon	Atrazine	80 %	28
	Acetamiprid		
	Difenoconazole		
P-doped biochar from corn straw	Triazine	79.6 mg g ⁻¹	35
Corn/starch-based mesoporous activated carbon (ACS)	Pyraclostrobin	66.2 mg g ⁻¹	36
Microporous starch immobilized laccase	Atrazine	0.2527 mg g ⁻¹	37
	Prometryn	0.1323 mg g ⁻¹	
Iron-starch modified with 3,5-diaminobenzidine and (3-aminopropyl) triethoxysilane	Isobenzan	0.00075 mg g ⁻¹	31
	Endosulfan	0.002 mg g ⁻¹	
	Chlordane	0.001 mg g ⁻¹	

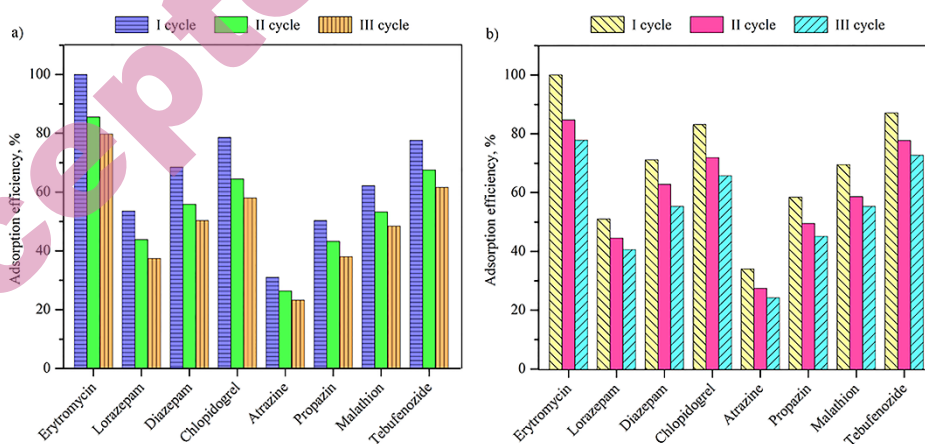


Fig. 6. Adsorption efficiency of amino starch derivatives SC (a) and SH (b) for the removal of selected pharmaceuticals and pesticides through three reuse cycles

CONCLUSION

In this study, an environmentally acceptable and economically viable method was developed for the modification of starch by introducing nitrogen-rich

compounds (melamine, cysteine, and histidine). Obtained amino-starch derivatives were used as adsorbents for the removal of selected pharmaceuticals and pesticides from aqueous solutions. Structural, morphological, and surface analysis have confirmed the success of the modification and an increase in the adsorption efficiency of amino-starch derivatives compared to unmodified starch has been achieved. Additional modification of amino-starch with clay and diatomaceous earth did not have a significant impact, compared to the basic modification, probably due to the coating of the starch surface with parts of clay or diatomaceous earth, i.e. reduced porosity of the material and less available sites for adsorption. Starch modified with histidine proved to be the most efficient material for the adsorption of investigated pharmaceuticals and pesticides, with the possibility of reuse in three adsorption cycles. The application of newly prepared adsorbents in real water samples (surface, ground, and wastewater) has shown that the matrix of real water had no significant effect on the adsorption efficiency, indicating that amino-starch derivatives, as a cheap and effective adsorbent could be considered as promising materials for wastewater treatment.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/13054>, or from the corresponding author on request.

Acknowledgements: This research was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-65/2024-03/200135 and 451-03-66/2024-03/200287).

ИЗВОД

АМИНО-СКРОБНИ ДЕРИВАТИ ЗА АДСОПЦИЈУ СПЕЦИФИЧНИХ ФАРМАЦЕУТИКА И ПЕСТИЦИДА ИЗ ЗАГАЂЕНИХ ВОДА: ИСПИТИВАЊЕ ВЕШТАЧКИ ОНЕЧИШЋЕНИХ И РЕАЛНИХ УЗОРАКА ВОДА

НАТАША ПАЛИЋ¹, МАРИЈА ВУКЧЕВИЋ², МАРИНА МАЛЕТИЋ¹, МИЉАНА МИРКОВИЋ³, МИРЈАНА РИСТИЋ², АЛЕКСАНДРА ПЕРИЋ ГРУЊИЋ² И КАТАРИНА ТРИВУНАЦ²

¹Иновациони Центар Технолошко-металуришког факултета, Карнегијева 4, 11000 Београд, Србија,

²Универзитет у Београду, Технолошко-металуришког факултета, Карнегијева 4, 11000 Београд, Србија,

и ³Универзитет у Београду, Институт за нуклеарне науке Винча – Институт од националног значаја Републике Србије, Мике Пешковића Аласа 12–14, Винча, 11000 Београд, Србија.

У овој студији испитана је могућност употребе модификованог кромпировог скроба, са хемијским агенсима који садрже азот (меламин, цистеин и хистидин) као зеленог адсорбента за уклањање лекова и пестицида из воде. Испитан је и утицај додатне модификације аминокроба глином и дијатомејском земљом. Ефекат примењене модификације на структурна, површинска и морфолошка својства одређен је FTIR, XRD и SEM анализом, док су адсорпциона својства припремљених адсорбента одређена кроз ефикасност уклањања изабраних загађујућих материја из спајкованих и реалних узорак воде. Ефикасност припремљених аминокрובה за адсорпцију лекова и пестицида

смањује се по следећем редоследу: скроб-хистидин>скроб-цистеин>скоб-меламин, уз нешто бољу ефикасност свих материјала за адсорпцију лекова. Додатна модификација аминок-скрובה глином/дијатомејском земљом није допринела повећању ефикасности адсорпције. Утврђено је да матрица реалних узорака воде утиче на ефикасност адсорпције до 10 %, што указује на обећавајући потенцијал за примену аминок-скрובה као јефтиног и ефикасног адсорбента за третман отпадних вода. Такође, адсорбенти скроб-хистидин и скроб-цистеин су показали могућност поновне употребе кроз три циклуса адсорпције.

(Примљено 19. септембра 2024; ревидирано 3. децембра 2024; прихваћено 10. јануара 2025.)

REFERENCES

- O. I. González Peña, M. Á. López Zavala, H. Cabral Ruelas, *Int. J. Environ. Res. Public Health* **18** (2021) 5 (<http://doi.org/10.3390/ijerph18052532>)
- M. Z. Hosain, S. M. Lutful Kabir, M. M. Kamal, *Vet. World* **14** (2021) 210 (<http://doi.org/10.14202/VETWORLD.2021.210-221>)
- A. J. Ebele, M. Abou-Elwafa Abdallah, S. Harrad, *Emerg. Contam.* **3** (2017) 1 (<http://doi.org/10.1016/j.emcon.2016.12.004>)
- K. H. Kim, E. Kabir, S. A. Jahan, *Sci. Total Environ.* **575** (2017) 525 (<http://doi.org/10.1016/j.scitotenv.2016.09.009>)
- N. Karić, M. Vukčević, M. Maletić, S. Dimitrijević, M. Ristić, A. Perić Grujić, K. Trivunac, *Int. J. Biol. Macromol.* **241** (2023) 124527 (<http://doi.org/10.1016/j.ijbiomac.2023.124527>)
- R. Natarajan, K. Saikia, S. K. Ponnusamy, A. K. Rathankumar, D. S. Rajendran, S. Venkataraman, D. B. Tannani, V. Arvind, T. Somanna, K. Banerjee, N. Mohideen, V. K. Vaidyanathan, *Chemosphere* **287** (2022) 131958 (<http://doi.org/10.1016/j.chemosphere.2021.131958>)
- Y. Koriche, M. Darder, P. Aranda, S. Semsari, E. Ruiz-Hitzky, *Dalton Transactions*. 43 (2014) 10512-10520 (<http://doi.org/10.1039/c4dt00330f>)
- Z. C. Yu, H. L. He, J. Lin, *Advanced Materials Research*. 821-822 (2013) 535-539. (<http://doi.org/10.4028/www.scientific.net/AMR.821-822.535>)
- S. Lawchoochaisakul, P. Monvisade, P. Siriphannon, *Carbohydr. Polym.* **253** (2021) 117230 (<http://doi.org/10.1016/j.carbpol.2020.117230>)
- H. Mittal, S. M. Alhassan, S. S. Ray, *J. Environ. Chem. Eng.* **6** (2018) 6 (<http://doi.org/10.1016/j.jece.2018.11.010>)
- H. Zhu, S. A. Xu, *RSC Adv.* **8** (2018) 32 (<http://doi.org/10.1039/c8ra01846d>)
- L. Li, L. Liao, Y. Ding, H. Zeng, *RSC Adv.* **7** (2017) 17 (<http://doi.org/10.1039/C6RA24971J>)
- H. Zaitan, D. Bianchi, O. Achak, T. Chafik, *J. Hazard Mater.* **153** (2008) 1-2 (<http://doi.org/10.1016/j.jhazmat.2007.09.070>)
- P. Pookmanee, A. Wannawek, S. Satienperakul, R. Putharod, N. Laorodphan, S. Sangsrichan, S. Phanichphant, *Materials Science Forum.* **872** (2016) 211 (<http://doi.org/10.4028/www.scientific.net/MSF.872.211>)
- D. E. González-Santamaría, A. Justel, R. Fernández, A. I. Ruiz, A. Stavropoulou, J. D. Rodríguez-Blanco, J. Cuevas, *Appl Clay Sci.* **212** (2021) 106223 (<http://doi.org/10.1016/j.clay.2021.106223>)
- H. Meradi, L. A. Hadi, W. Ghabeche, L. Bahloul, *Int. J. Eng. Sci. Technol* **9** (2018) ISSN: 1737-9296

17. L. A. Muñoz, F. Pedreschi, A. Leiva, J. M. Aguilera, *J. Food Eng.* **152** (2015) 65 (<http://doi.org/10.1016/j.jfoodeng.2014.11.017>)
18. S. L. Abdullahi, A. A. Audu, *Chem. Search Journal.* **8** (2017) 2 (<https://www.ajol.info/index.php/csj/article/view/166246>)
19. P. Yuan, D. Liu, D. Y. Tan, K. K. Liu, H. G. Yu, Y. H. Zhong, A. H. Yuan, W. B. Yu, H. P. He, *Microporous and Mesoporous Materials.* **170** (2013) 9 (<http://doi.org/10.1016/j.micromeso.2012.11.030>)
20. S. Elbasaney, A. Baraka, M. Gobara, Y. H. El-Sharkawy, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **245** (2021) 118941 (<http://doi.org/10.1016/j.saa.2020.118941>)
21. A. A. Galhoum, A. A. Atia, M. G. Mahfouz, S. T. Abdel-Rehem, N. A. Gomaa, T. Vincent, E. Guibal, *J. Mater. Sci.* **50** (2015) 7 (<http://doi.org/10.1007/s10853-015-8845-z>)
22. A. B. True, K. Schroeck, T. A. French, C. A. Schmuttenmaer, *J. Infrared Millim. Terahertz Waves.* **32** (2011) 5 (<http://doi.org/10.1007/s10762-010-9645-9>)
23. A. Ansari Mojarad, S. Tamjidi, H. Esmaeili, *Int. J. Environ. Anal. Chem.* **102** (2022) 19 (<http://doi.org/10.1080/03067319.2020.1845665>)
24. G. Aschermann, C. Schröder, F. Zietzschmann, M. Jekel, *Chemosphere* **237** (2019) 124415 (<http://doi.org/10.1016/j.chemosphere.2019.124415>)
25. R. Guillossou, J. Le Roux, R. Mailler, C. S. Pereira-Derome, G. Varrault, A. Bressy, E. Vulliet, C. Morlay, F. Nauleau, V. Rocher, J. Gasperi, *Water Res.* **172** (2020) 115487 (<https://doi.org/10.1016/j.watres.2020.115487>)
26. F. Zietzschmann, C. Stützer, M. Jekel, *Water Res.* **92** (2016) 180 (<http://dx.doi.org/10.1016/j.watres.2016.01.056>)
27. B. Pan, D. Zhang, H. Li, M. Wu, Z. Wang, B. Xing, *Environ. Sci. Technol.* **47** (2013) 14 (<http://doi.org/10.1021/es4008933>).
28. B. Zhang, Y. Jin, X. X. Huang, S. Tang, H. Chen, Y. Su, X. Yu, S. Chen, G. Chen, *Chem. Eng. J.* **450** (2022) 138264 (<http://doi.org/10.1016/j.cej.2022.138264>)
29. Q. Shen, M. H. Xu, T. Wu, G. X. Pan, P. S. Tang, *Chemical Papers* **76** (2022) 123 (<http://doi.org/10.1007/s11696-021-01839-w>)
30. A. K. Mohamed, M. E. Mahmoud, *Carbohydr Polym.* **245** (2020) 116438 (<http://doi.org/10.1016/j.carbpol.2020.116438>)
31. D. A. Mustofa, J. Gamonchuang, R. Burakham, *Analytical Sciences* **37** (2021) 11 (<http://doi.org/10.2116/analsci.21P034>)
32. M. Bouhedda, S. Lefnaoui, S. Rebouh, M. M. Yahoum, *Chemometr. Intell. Lab. Syst.* **193** (2019) 103843 (<http://doi.org/10.1016/j.chemolab.2019.103843>)
33. S. Kang, W. Liu, Y. Wang, Y. Wang, S. Wu, S. Chen, B. Yan, X. Lan, *J. Taiwan Inst. Chem. Eng.* **135** (2022) 104383 (<http://doi.org/10.1016/j.jtice.2022.104383>)
34. A. U. Itodo, I. S. Eneji, T. T. Weor, *J. Chem Soc. Nigeria.* **43** (2018) 4 (<https://journals.chemsociety.org.ng/index.php/jcsn/article/view/216/267>)
35. F. Suo, X. You, Y. Ma, Y. Li, *Chemosphere* **235** (2019) 918 (<http://doi.org/10.1016/j.chemosphere.2019.06.158>)
36. F. Suo, X. Liu, C. Li, M. Yuan, B. Zhang, J. Wang, Y. Ma, Z. Lai, M. Ji, *Int. J. Biol. Macromol.* **121** (2019) 806 (<http://doi.org/10.1016/j.ijbiomac.2018.10.132>)
37. X. Chen, Q. Zhou, F. Liu, Q. Peng, Y. Bian, *Environ. Technol. Innov.* **21** (2021) 101235 (<http://doi.org/10.1016/j.eti.2020.101235>).