Original scientific article

A GREEN ADSORBENT BASED ON WHEAT STARCH FOR REMOVAL OF SELECTIVE ORGANIC POLLUTANTS FROM AQUEOUS SOLUTIONS

Nataša Karić[1], Marija Vukčević[2], Marina Maletić[1], Mirjana Ristić[2], Aleksandra Perić-Grujić[2], Katarina Trivunac[2]

[1]Innovation Center of Faculty of Technology and Metallurgy, 11120 Belgrade, Serbia
[2]University of Belgrade, Faculty of Technology and Metallurgy, 11120 Belgrade, Serbia

Abstract

The objective of this study was to evaluate the adsorption efficiency of a cationic functionalized wheat starch, obtained with betaine hydrochloride and glycidyl trimethylammonium chloride by an environmentally friendly process without the use of organic solvents. Surface functional groups of samples were characterized by Fourier transform infrared spectroscopy, the morphology of the materials was examined using scanning electron microscopy, the nitrogen content was determined by elemental analysis, while UV-VIS spectroscopy and liquid chromatography-tandem mass spectrometry were used for adsorption investigation. The efficiency of obtained cationic starches to adsorb the anionic and cationic dyes, as well as selected pharmaceuticals and pesticides was investigated. Adsorption experiments were performed in a batch system to determine the effect of contact time, initial concentration, and pH of the solution on the removal efficiency of crystal violet dye, which was chosen as the model for the detailed study of adsorption. Pseudo-first and pseudo-second order models were used to examine the adsorption kinetic, while Langmuir and Freundlich isotherm models were applied to equilibrium adsorption data. The results showed that environmentally and economically acceptable adsorbents prepared in this study could be effective in removing the examined organic pollutants.

Keywords: eco-friendly process, modification, starch, adsorption, organic pollutants.

Introduction

The production and consumption of chemical products by consumers are associated with growing environmental pollution and negative impacts on the health of the population. This growing environmental pollution that has attracted significant global scientific attention, in addition to the activities of the chemical and pharmaceutical industries, can be attributed to other anthropogenic activities such as urbanization, mining, agriculture, and domestic activities that also largely contribute to the higher pollution index (Wen et al., 2017). Global water pollution with organic pollutants is one of the biggest challenges of the 21st century. Most of these organics are only partially removed in conventional wastewater treatment plants, and many of these pollutants are released into the environment and can be found in their various parts. Due to the ecotoxicological effects, bioaccumulation, and carcinogenic effects of organic pollutants or their degradation products on the environment and humans, the wastewater must be properly treated before being discharged into the environment (Ge et al., 2016). The adsorption technique has proven to be one of the most attractive methods for wastewater treatment due to its simplicity, speed, efficiency, and availability of cheap adsorbents based on polysaccharides, such as starch, cellulose, chitin, chitosan, and lignin (Lawchoochaisakul et al., 2020).

The aim of this work was to evaluate the possibility of using cationic starches obtained by an environmentally friendly process as adsorbents to remove selected organic pollutants from aqueous solutions. Two starch derivatives were used, starch modified with betaine hydrochloride (CSt-B) and glycidyl trimethylammonium chloride (CSt-G). The adsorption efficiency of anionic (methyl orange, MO, and alizarin red S, ARS) and cationic (crystal violet, CV, and methylene blue, MB) dyes, as well as selected pesticides (imidacloprid, acetamiprid, dimethoate, carbamazepine, atrazine, propazine, malathion, tebufenozide) and pharmaceuticals (metabolites of metamizole 4AAA and 4FAA, lorazepam, diazepam, and clopidogrel) was also investigated. Based on the obtained results for the efficiency of absorption, as well as due to the smaller number of works dealing with its removal from wastewater, crystal violet dye was chosen as a model for a detailed study of adsorption. In order to determine the optimal reaction conditions, the kinetics of adsorption, adsorption isotherms, as well as the influence of the initial pH values were examined.

Materials and Methods

Wheat starch was purchased from Žito Promet, Serbia (moisture content ≤15.0%, ash content 0.46–0.55%, carbon content - 39.96%, and hydrogen content - 21.3%).

The modification of wheat starch was performed by a dry process of mixing starch with a cationic reagent in the presence of plasticizer and reaction catalysts according to the procedure described earlier (Karić et al. 2021).

Surface structure and morphology were studied by scanning electron microscopy (FE-SEM, TESCAN Mira3 XMU), while Fourier-transform infrared spectroscopy was used for the structural characterization of the materials (Nicolet iS10 spectrometer, Thermo Scientific).

The efficiency of dye adsorption was investigated at a constant adsorbent mass (0.1 g), initial concentration (50.0 mg dm^{-3}) and solution volume (50.0 mL) for 180 min. The concentration of the dye in the solution was analyzed using a UV-VIS spectrophotometer. The adsorption efficiency of pesticides and pharmaceuticals was tested at a constant adsorbent mass (0.05 g), initial concentration (500.0 mg dm^{-3}) and solution volume (50.0 mL) for 180 min. The concentration of tested pesticides and pharmaceuticals in the solution was analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). The influence of different initial concentrations (25.0 to 500.0 mg dm^{-3}) and initial pH of the CV dye solution (25.0 mg dm^{-3}, pH adjusted to 2-9) on the adsorption efficiency was determined at a constant mass of adsorbent (0.05 g) and the volume of the solution (25.0 mL) during 180 min. The kinetics of CV adsorption of the dye was investigated in the interval from 5 to 180 min at constant adsorbent mass (0.2 g), solution volume (100.0 mL) and initial concentration (50.0 mg dm^{-3}).

The adsorption capacity, q (mg g^{-1}) and the removal efficiency, R (%) of selected pollutants from aqueous solutions can be calculated according to the equations (1) and (2) (Lin et al., 2017), respectively:

$$q = \left(\frac{C_0 - C_t}{m}\right) \cdot V \quad (1)$$

$$\% R = \left(\frac{C_0 - C_t}{C_0}\right) \cdot 100 \quad (2)$$

where C_0 and C_t (mg dm^{-3}) are the concentration of an organic pollutant at the initial time and after time t (min), V is the volume of solution (cm^3), and m is the amount of the adsorbent (g).

The nonlinear form of Langmuir model (Langmuir, 1918) and Freundlich model (Freundlich, 1906) are expressed by the equations (3) and (4), respectively:

$$q_e = \frac{q_{max} \cdot K \cdot C_e}{1 + K \cdot C_e} \quad (3)$$

$$q_e = K_f \cdot C_e^{1/n} \quad (4)$$

where q_e is the equilibrium adsorption capacity of the adsorbent (mg g^{-1}), q_{max} is the maximum adsorptive capacity of the adsorbent (mg g^{-1}), and C_e is the equilibrium concentration after adsorption (mg dm^{-3}), K is the Langmuir isotherm constant which describes the affinity between pollutants and adsorbents, K_F is Freundlich adsorption equilibrium constant which positively related to the adsorption capacity (dm^3 g^{-1}) and *1/n* is the constant of adsorption intensity and describes surface heterogeneity.

The pseudo-first order model (Lagergren, 1898) and the pseudo-second order model (Ho & Mckay 1999) were expressed by the equations (5) and (6), respectively:

$$q_t = q_e \cdot \left(1 - e^{-k_1 \cdot t}\right) \quad (5)$$

$$q_t = q_e - \left(\frac{1}{q_e} - k_2 \cdot t\right)^{-1} \quad (6)$$

where q_t is the amount of pollutant adsorbed at the time t (mg g^{-1}), q_e is the adsorption quantity at equilibrium (mg g^{-1}), k_1 is the pseudo-first-order kinetic rate constant (min^{-1}), and k_2 is the pseudo-second-order kinetic rate constant (mg g^{-1} min^{-1}).

Results and discussion

The FTIR spectra of unmodified starch and cationic starch are shown in Fig. 1.

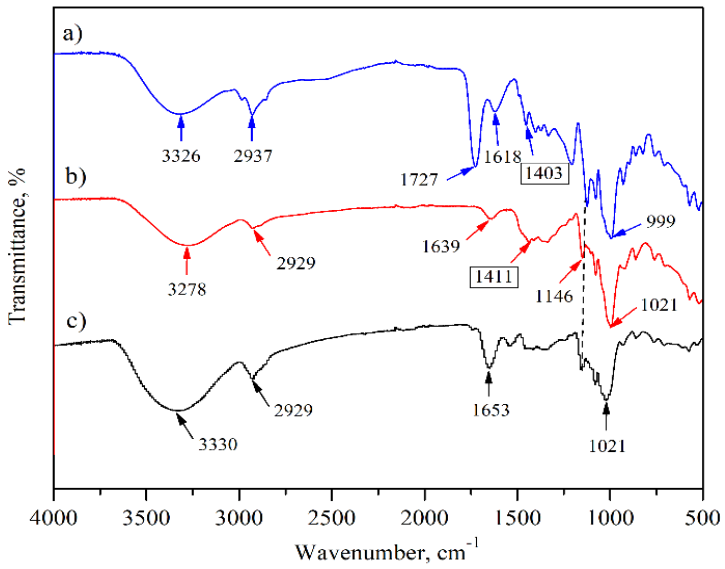

Figure 1. FTIR spectra of a) CSt-B, b) CSt-G, and c) unmodified starch

All the spectra showed a typical peak of starch backbone: wide hydroxyl bands at 3330, 3326, and 3278 cm^{-1}, the peaks at about 2929 and 2937 cm^{-1} which belong to C–H stretching vibrations, the peaks at 1653, 1618, and 1639 cm^{-1} for H–O–H bending vibration, the signal at 1146 cm^{-1} of the C–O stretching vibrations of the glucose unit, the peaks at 1021 and 999 cm^{-1} attributed to the C–O–C stretching vibrations of the anhydroglucose unit (AGU) (Lawchoochaisakul et al., 2021). The

absorption peak at 1727 cm^{-1} at the FTIR spectra of CSt-B (Fig. 1a) was assigned to the stretching vibration of C=O of the ester carbonyl group, indicating the formation of ester bonds between starch and BHC. In addition to the characteristic peaks for starch structure (Fig. 1a) the presence of additional bands at 1403 and 1411 cm^{-1} on cationic starches spectra (Fig. 1a and 1b) are attributed to the stretching vibration of C–N bonds from quaternary ammonium cationic group (Nasir et al., 2020). The SEM micrographs of the unmodified starch and starch materials after cationization are shown in Fig. 2.

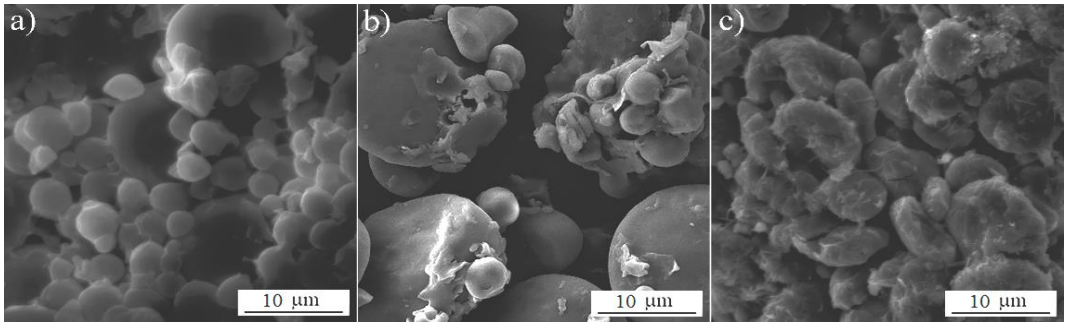

Figure 2. SEM micrographs of a) unmodified starch, b) CSt-B, and c) CSt-G

Fig. 2a shows that the surface of unmodified starch granules is smooth and the granules are spherical or oval. Micrographs of cationic starches (Fig. 2b and 2c) show that the surface of the granules became uneven, with protrusions and holes. Granules partially (Fig. 2b) or completely (Fig. 2c) lose their clear shape, due to partial or complete gelatinization and agglomeration of granules after cationization (Liu et al., 2017). The results of the efficiency of removing MO, CV, ARS, and MB dyes from individual solutions are shown in Fig. 3a, while the results of the efficiency of removing selected pharmaceuticals and pesticides from the multicomponent solution are shown in Fig. 3b.

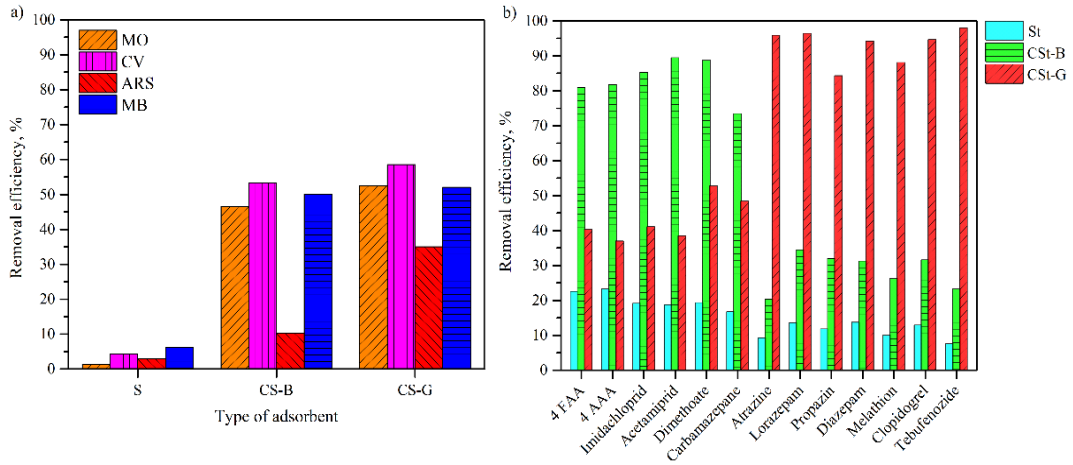

Figure 3. Adsorption efficiency of examined materials toward a) anionic and cationic dyes and b) pharmaceuticals and pesticides

Fig. 3a shows the comparative results of the efficiency of CSt-G and CSt-B in removing different dyes. The tested materials proved to be the most effective adsorbents for the removal of cationic dye, CV. Both materials showed similar efficiency in removing MB dye, while the removal efficiency of MO, CV, and ARS was slightly better for the CSt-G material. The lowest efficiency was obtained for the removal of ARS dye, especially in the case of adsorption with CSt-B. Fig. 3b shows that CSt-B material was more effective in removing most of the tested pharmaceuticals, while CSt-G material was more effective in removing lorazepam, diazepam, and clopidogrel. Also, CSt-G material proved to be more effective in removing all tested pesticides compared to CSt-B material. Considering that polarity of selected pesticides and pharmaceuticals decreases along the X-axis (from the most polar

4-AAA to the less polar tebufenozide), it was noticed that CSt-B showed higher efficiency for the removal of polar compounds, while CSt-G was more efficient in the removal of nonpolar compounds. The influence of the initial pH value of the solution, as well as adsorption time, on the removal efficiency of CV, is given in Fig. 4a. Removal efficiency increases with pH, and the highest removal efficiency for both materials was achieved at pH 9. The adsorption capacity of both types of adsorbents increases significantly in the first 60 minutes of adsorption (Fig. 4b), almost reaching the equilibrium, after which increases slightly up to 180 min. The fast adsorption in the first 15 min can be explained in terms of the high concentration gradient and the availability of a large number of active sites for the adsorption. The pseudo-second order model has a greater ability to describe the kinetic behavior of the adsorption process, indicating that adsorption occurs through the chemisorption reaction (Baloo et. al., 2021).

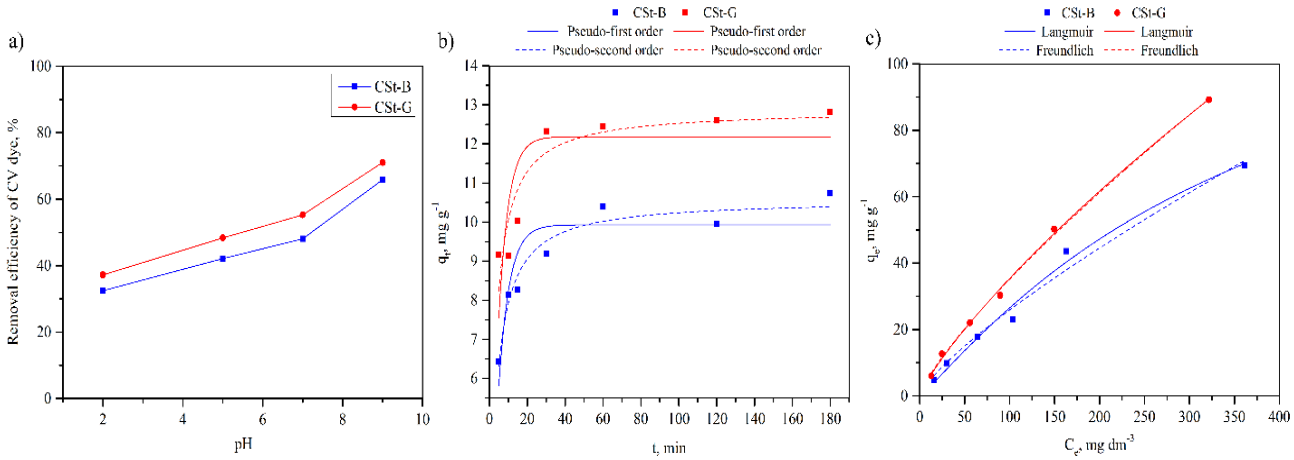

Figure 4. Effect of pH solution (a), time (b), and initial concentration (c) on the removal efficiency of CV dyes

Fig. 4c shows that equilibrium adsorption capacity increases with an initial concentration on CV solution, although the characteristic plateau was not reached in the examined concentration range. Also, both Langmuir and Freundlich adsorption isotherms equally well describe the adsorption of CV on both types of materials.

Conclusion

Modified starch derivates, prepared with betaine hydrochloride (CSt-B) and glycidyltrimethylammonium chloride (CSt-G), were used as adsorbents for the removal of different organic pollutants from water. An increase in the removal efficiency of selected organic pollutants indicated that applied modification has a positive effect on starch adsorption properties. For the adsorption of pesticides and pharmaceuticals, CSt-B showed higher affinity to adsorb more polar, and CSt-G less polar compounds. On the other hand, similar behavior in the adsorption of dyes was observed for both CSt-G and CSt-B samples, with sample CSt-G being slightly more efficient. Adsorption of crystal violet onto both modified starch was highly dependent on solution pH, reaching its maximum at pH 9. For both cationic starches, adsorption equilibrium was attained very rapidly, after 60 minutes. The kinetic data were well described by the pseudo-second order model, while the data obtained from the isotherm study fit well with both Langmuir and Freundlich models. The results of this study indicate that the cationization of wheat starch by the process without the use of expensive and toxic chemicals can be successfully used for the preparation of effective and eco-friendly adsorbents to remove organic pollutants from aqueous solutions.

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