FLY ASH MODIFIED WASTE COTTON AND COTTON-POLYESTER YARNS FOR REMOVAL OF HEAVY METALS FROM WATER

M. Maletić[1], A. Lazović[2], N. Karić[1], M. Vukčević[2], K. Trivunac[2], M. Ristić[2] and A. Perić-Grujić[2]

[1]*Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia. (mvukasinovic@tmf.bg.ac.rs)*
[2]*University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia.*

ABSTRACT
Using two types of industrial waste materials (yarns and fly ash), adsorbents for removing heavy metal ions from water were obtained. To improve the adsorption efficiency of cotton and cotton-polyester yarns, modification using fly ash and sodium alginate as a binder, was applied. Characterization of materials was performed by Scanning electron microscopy and Fourier transform infrared spectroscopy, while the concentration of lead and cadmium ions was determined using atomic absorption spectroscopy. The modification of the material has contributed to an increase in the adsorption efficiency of lead and cadmium by up to twice in comparis onto the unmodified materials. It was found that the kinetics of the metal adsorption process can be better described by a second-order pseudo model. The results showed that by combining two types of industrial waste, cotton and cotton/polyester yarns and fly ash, highly efficient adsorbents for removing lead and cadmium from aqueous solutions are obtained.

INTRODUCTION
Heavy metals reach the environment through the industrial activities of metallurgy, nuclear industry, batteries, leather, pesticides, fertilizers, oil and textile industries. Unlike organic pollutants, heavy metal ions in the aquatic environment have a great tendency to bioaccumulate, because they do not decompose naturally, which can cause various health problems in humans. Toxicity can be manifested even at very low concentrations, when organ damage, growth retardation, headaches, mental disorders, skin diseases, and nervous system dysfunction can occur [1]. Therefore, the removal of heavy metals from wastewater is of great importance to reduce their harmful effects. Among conventional techniques used to remove heavy metals from water, adsorption is most effective because other techniques have inherent limitations such as high sludge production, low efficiency, sensitive working conditions, and costly disposal. The adsorption method provides flexibility in design, ease of application, economy, high-quality treated effluent, reversibility of the process, and reuse of the adsorbent [2]. From the aspect of environmental protection, the conditions for wastewater discharge are becoming more stringent, while the application of environmentally and economically acceptable adsorbents for wastewater treatment is a great challenge today. Therefore, in this study, the possibility of using easily available waste materials as efficient adsorbents for removing heavy metal ions from aqueous solutions was investigated. Fly ash, obtained from thermal power plants as a by-product, was used to modify and improve the adsorption efficiency of cotton and cotton-polyester yarns, which were obtained as waste from the textile industry. Lead and cadmium have been used, as models to determine the effectiveness of unmodified and modified materials in removing heavy metal ions.

METHODS

Waste cotton (C) and cotton-polyester yarns (CP) (50% cotton-50% polyester) were obtained from the production processes of the textile factory SIMPO Dekor (Vranje, Serbia). The materials were modified in a two-cycle process. 0.1 g of material was weighed and immersed in 4 ml of a mixture of 0.5% aqueous sodium alginate solution and 0.1 g of fly ash for 10 minutes. Thereafter, the materials were dried at 60 °C for 1 h. After the second modification cycle, the materials were dried at 60 °C overnight, and the modified materials were labelled as C-alg-FA and CP-alg-FA, for modified cotton and cotton-polyester, respectively. The morphological characteristics of the surface of unmodified and modified materials were examined by scanning electron microscopy (SEM), while examination of the content of functional groups on the surface of the material was performed by Fourier transform infrared spectroscopy (FTIR). The adsorption efficiency of Pb and Cd from aqueous solutions using unmodified and modified yarns was tested in a batch system and at room temperature. The yarn samples, weighing 0.02 g, were immersed in 20 ml of an aqueous solution of metal ions with a concentration of 10 mg dm^{-3} and stirred constantly at 150 rpm for 3 h. Metal ion concentrations after adsorption were determined by atomic absorption spectroscopy. The adsorption efficiency (%A) of the tested materials in the removal of metal ions was calculated using the following equation (1):

$$\% \text{A} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where C_e is the equilibrium and C_0 is the initial concentration of metal ions in solution (mg dm^{-3}).
The two kinetic models, the pseudo-first order model (equation (2)) and the pseudo-second order model (equation (3)) were used to calculate the adsorption rate [3].

$$q_t = q_e \cdot \left(1 - e^{-k_1 \cdot t}\right) \tag{2}$$

$$q_t = q_e - \left(\frac{1}{q_e} - k_2 \cdot t\right)^{-1} \tag{3}$$

where q_t is the amount of metal ions 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 SEM micrographs of the unmodified cotton and cotton-polyester yarns and modified with fly ash are shown in Figure 1.

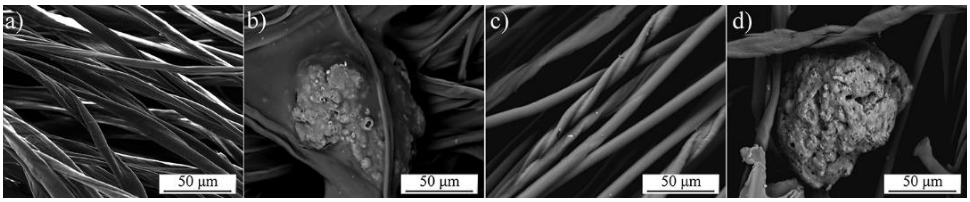

Figure 1. SEM micrographs of a) cotton yarns, b) C-alg-FA, c) cotton-polyester yarns, and d) CP-alg-FA.

It can be seen that the untreated cotton yarns (Figure 1a) are intertwined, with the cotton fibers spirally twisted with a relatively smooth surface. Figure 1c shows the morphology of unmodified cotton-polyester yarns, where in addition to the cotton component, the presence of polyester fibers with a uniform tubular structure and smooth surface is observed. Fly ash is incorporated between cotton and polyester component (Figures 1b and 1d), and bound to them with sodium alginate, which acts as a binding agent.

FTIR spectra of modified materials are shown in Figure 2a. The presence of a wide absorption band at 3300 cm^{-1} in the structure of all materials originates from the vibration of the O-H bond in the hydroxyl group, while the peak at 2900 cm^{-1} is the characteristic peak of the stretching vibration of the C-H bond in the methyl or methylene group of cellulose molecules. The peak at 1612 cm^{-1} in the spectra of samples C and C-alg-FA may be related to the presence of water in the cotton fibers. The adsorption peaks at 1427 and 1406 cm^{-1} are associated with the CH_2 symmetric bending of the cellulose while the peaks at 1312 and 1335 cm^{-1} originate from the bending vibrations of the C-H and C-O groups of the aromatic rings in cellulose structure. The intense band at 1021 cm^{-1} in spectra of all materials is related to the C=O and C-O stretching vibrations of the polysaccharide in cellulose, while the peak at 895 cm^{-1} indicates the presence of β-glycosidic linkages between monosaccharides [4]. The FTIR spectra of CP and CP-alg-FA, compared to the spectra of cotton yarns, have additional absorption peaks at 1711 cm^{-1} and 1234 cm^{-1}, which indicates the presence of ester groups in polyester chains [5].

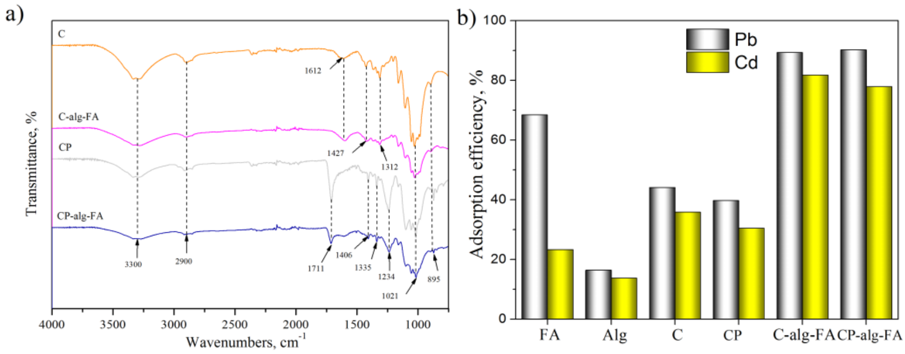

Figure 2. FTIR spectra (a) and adsorption efficiency (b) of unmodified and modified materials.

Figure 2b shows the efficiency of the modified samples (C-alg-FA and CP-alg-FA) in removing Pb and Cd from aqueous solutions, compared with the adsorption efficiency of unmodified samples (C and CP), alginate particles (Alg), and fly ash (FA). It can be noted that the modification of the material increased the efficiency of Pb and Cd removal almost twice. The removal efficiency of both metals on the modified materials ranged from 80 to 90%, with a slightly higher removal efficiency of Pb. High efficiency in the removal of metal ions may be due to the presence of a large number of hydroxyl and carboxyl groups on the surface of the modified materials.

Graphs of pseudo-first and pseudo-second-order models are given in Figure 3, while the kinetic constants and correlation coefficients for Pb and Cd adsorption are shown in Table 1. The pseudo-first order and pseudo-second order equations were used to evaluate the adsorption kinetic data and investigate the adsorption mechanism.

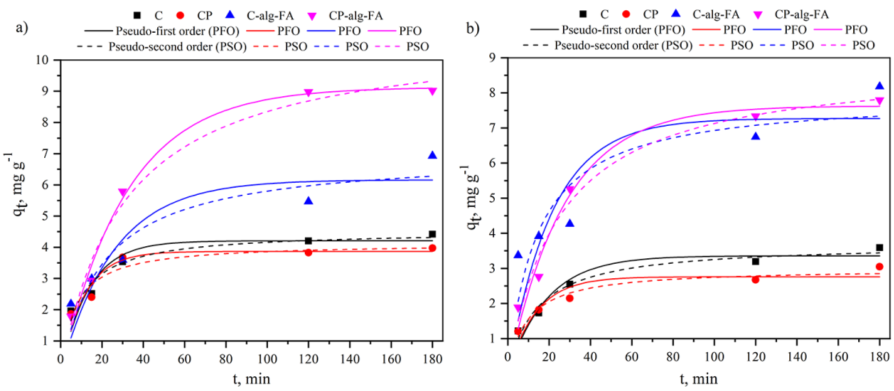

Figure 3. Nonlinear kinetic adsorption models of metals Pb (a) and Cd (b) on tested samples.

Based on the results of kinetic models, it can be seen that the process of metal adsorption on all tested materials was relatively fast and that equilibrium was reached at about 30 min for Cd and 60 min for Pb. The highest adsorption capacity was achieved using C-alg-FA material for Pb removal. Also, by comparing the correlation coefficient (R^2), it can be concluded that the pseudo-second order model has a greater ability to describe the kinetic behaviour of the adsorption process, which means that the dominant mechanism of adsorption is chemisorption.

Table 1. Kinetic constants and correlation coefficients for Pb and Cd adsorption on samples C, C-alg-FA, CP, and CP-alg-FA.

Metal	Material	Pseudo-first order			Pseudo-second order		
		q_e, mg g^{-1}	k_1, min^{-1}	R^2	q_e, mg g^{-1}	k_2, g mg^{-1} min^{-1}	R^2
Pb	C	4.20	0.0743	0.818	4.52	0.0252	0.933
	C-alg-FA	6.16	0.0390	0.838	6.99	0.0069	0.888
	CP	3.86	0.0879	0.758	4.13	0.0339	0.852
	CP-alg-FA	9.13	0.0314	0.984	10.9	0.0029	0.975
Cd	C	3.35	0.0534	0.899	3.70	0.0189	0.955
	C-alg-FA	7.27	0.0468	0.526	7.91	0.0089	0.704
	CP	2.76	0.0743	0.800	2.99	0.0363	0.938
	CP-alg-FA	7.62	0.0367	0.967	8.87	0.0045	0.968

CONCLUSION

In this study, adsorbents based on waste industrial materials, yarns and fly ash, for the removal of lead and cadmium ions from aqueous solutions were successfully obtained. The adsorption properties of cotton and cotton-polyester yarns were improved by mixing with fly ash and sodium alginate as a binder. Structural and morphological characterization of the materials confirmed that the modification was successful. Adsorption results showed that all tested materials show slightly better efficiency of lead adsorption compared to cadmium. Also, the results show that the modification of waste yarns with fly ash has contributed to the increase in the efficiency of lead and cadmium ions removal almost twice.

Acknowledgment

This research was supported by the Science Fund of the Republic of Serbia, GRANT No 7743343, Serbian Industrial Waste towards Sustainable Environment: Resource of Strategic Elements and Removal Agent for Pollutants - SIW4SE.

REFERENCES

[1] Beni, A.A., and Esmaeili, A., Environ. Technol. Innov., 17 (2020) 0100503.
[2] Agarwal, R. M., and Singh, M., J. Water Reuse Desal., 230 (2019) 278.
[3] Lekniute-Kyzike, E., Bendoraitiene, J., Danilovas, P. P., and Zemaitaitis, A., Desalin. Water Treat., 57 (2016) 23728–23738.
[4] Portella, E. H., Romanzini, D., Angrizani, C. C., Amico, S. C., and Zattera, A. J., Mater. Res., (2016) 1-7.
[5] Jiang, S., Xia, Z., Farooq, A., Zhang, M., Li, M., and Liu, L., Cellulose, 28 (2021) 3235-3248.