WASTE MATERIALS AS ADSORBENTS FOR HEAVY METALS REMOVAL FROM WATER: COMPARATIVE ANALYSIS OF MODIFICATION TECHNIQUES

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Abstract: *This study aims to investigate the effect of alkalization and chemical coupling methods on the surface and adsorption properties of waste cotton and cotton/polyester yarns. The simple and cheap alkali treatment was performed using 10% and 18% NaOH solution, while the chemical coupling method involved combining cotton and cotton/polyester yarns and fly ash, using sodium carboxymethyl cellulose and sodium alginate as binders. Morphological and surface characteristics of unmodified and modified cotton and cotton/polyester yarns were analyzed by scanning electron microscopy and Fourier transform infrared spectroscopy, while adsorption properties were assessed by the removal of lead and cadmium ions from aqueous solution. It was found that chemical modification with 18% NaOH solution positively affected the adsorption properties of only cotton yarns, increasing the removal efficiency of lead ions up to 75%. On the other hand, modification with fly ash improves the adsorption properties of both, cotton and cotton/polyester yarns, increasing the efficiency in removing lead ions by using sodium carboxymethyl cellulose, and cadmium ions by using alginate as a binder. Using the chemical coupling method, effective adsorbents are obtained starting from waste yarn, which gives it added value, the amount of non-degradable waste material can be reduced and the criteria of a cleaner environment and circular economy can be met.*

Keywords: cotton, cotton/polyester, yarns, chemical modification, fly ash, heavy metals.

ADSORBENTI NA BAZI OTPADNIH MATERIJALA ZA UKLANJANJE TEŠKIH METALA IZ VODE: UPOREDNA ANALIZA TEHNIKA MODIFIKACIJE

Apstrakt: *Prediva pamuka i pamuk/poliestra, dobijena kao otpad iz tekstilne industrije, korišćena su kao adsorbenti za uklanjanje teških metala iz vode. U cilju poboljšanja adsorpcionih karakteristika ispitivanih prediva primenjen je jednostavan i jeftin postupak hemijske modifikacije korišćenjem 10% i 18% rastvora NaOH, kao i modifikacija otpadnih prediva kombinovanjem sa još jednim otpadnim materijalom, letećim pepelom, uz korišćenje natrijum alginata i natrijum karboksimetilceluloze kao veziva. Karakterizacija ispitivanih materijala je izvršena u cilju ispitivanja uticaja primenjenih metoda modifikacije na morfološke, površinske i adsorpcione karakteristike materijala. Analiza morfologije i površinskih karakteristika polaznih i modifikovanih materijala izvršena je korišćenjem skenirajuće elektronske mikroskopije i infracrvene spektroskopije sa Furijeovom transformacijom, dok su adsorpcione karakteristike materijala ispitane kroz efikasnost uklanjanja jona olova i kadmijuma iz vodenih rastvora. Utvrđeno je da hemijska modifikacija natrijum hidroksidom ne dovodi do* *značajnijeg poboljšanja adsorpcionih karakteristika materijala, osim u slučaju modifikacije pamučne pređe sa rastvorom 18% NaOH, pri čemu dolazi do povećanja efikasnosti uklanjanja jona olova do 75%. S druge strane, modifikacija otpadnih prediva letećim pepelom poboljšava njihove adsorpcione karakteristike, povećavajući efikasnost uklanjanja jona olova korišćenjem natrijum karboksimetil celuloze, odnosno jona kadmijuma korišćenjem natrijum alginata kao veziva.*

Ključne reči: pamuk, pamuk/poliestar, pređa, hemijska modifikacija, leteći pepeo, teški metali.

1. INTRODUCTION

The high toxicity, non-degradability, and bioaccumulation of heavy metals, their constant industrial production, and their presence in wastewater and drinking water represent threats to the environment and human health that require an urgent solution [1]. Of the heavy metals, lead (Pb(II)) and cadmium (Cd(II)) are often present in contaminated water, which even in very low concentrations can be very harmful to human health and the environment. Lead poisoning causes anemia, disorders of the central and peripheral nervous system, hallucinations, as well as damage to the renal, osteo skeletal and cardiovascular systems [2]. Cadmium poisoning causes disorders of kidney function, damage to the osteo skeletal, respiratory, reproductive, cardiovascular, hematological, and central nervous systems; and has carcinogenic effects [3, 4].

In addition to several methods used for water treatment, adsorption is currently the most attractive for the removal of heavy metal ions from polluted waters. The reason for this is the flexibility and simplicity of the process, labor costs, the possibility of adsorbent regeneration, and the ability to remove low concentrations of heavy metals from water [5]. Special attention is paid to the selection of adsorbent, which significantly contributes to all the mentioned advantages of the adsorption process [1]. In recent years, adsorbents based on different waste materials have been increasingly used, which through physical and chemical modification provide high adsorption capacity, fast adsorption equilibrium, and simple regeneration [5].

The global textile market is dominated by cellulosic cotton fibers and synthetic polyester fibers. The impact of these materials from production, consumption and final disposal on the environment is the subject of extensive research today. Due to the difficulty in recycling or adding value to the resulting textile waste, most textile waste is landfilled or incinerated, neither of which is environmentally sustainable [6]. Therefore, efforts are made to propose an easier and cheaper method to reduce the growing harmful effects of textile waste. One way of achieving that goal is the use of environmentally and economically acceptable modifications to convert these waste materials into adsorbents for wastewater treatment [7, 8]. Different physical and chemical modification techniques may be used to improve the adsorption properties of cellulosic-based materials. Physical treatments for surface modification, such as corona, dielectric barrier and plasma discharges, laser and UV (ultraviolet) irradiation [9-12] alter the structural and surface properties of the fibers without the use of chemical agents. On the other hand, chemical treatments are applied to alter the physicochemical and mechanical properties of fibers and to functionalize the fiber surface by changing the type and amount of functional groups, which act as active sites for adsorption. The most commonly used chemical modification methods are oxidation, alkalization (mercerization), and chemical coupling methods.

This study aims to investigate the effect of alkalization and chemical coupling methods on the surface and adsorption properties of waste cotton and cotton/polyester yarns. The simple and cheap alkali treatment was performed using 10% and 18% NaOH solution, while the chemical coupling method involved combining cotton and cotton/polyester yarns and fly ash, using sodium carboxymethyl cellulose and sodium alginate as binders. Fly ash is another industrial waste material generated in large quantities and requires safe disposal [13]. Fly ash is produced in the coal combustion chamber in thermal power plants and contains particles in the form of fine glass powder with a size of 0.5 to 100 μm, which rises with the flue gases [14]. In recent years, awareness has been raised about the need to reuse fly ash, and numerous kinds of research have been conducted in the field of using fly ash to remove heavy metals and organic compounds from wastewater [15-17]. Therefore, with the intention of reusing waste materials and meeting the demands of a cleaner environment and circular economy, two kinds of waste materials, cotton and cotton/polyester yarns and fly ash, were combined for obtaining an efficient adsorbent for purification of wastewater polluted with lead and cadmium ions.

2. EXPERIMENTAL

2.1. Preparation of adsorbents

As starting materials for adsorbents preparation, two kinds of waste materials were used: cotton (P) and cotton/polyester (50% cotton-50% polyester) (P/PES) yarns, obtained from the production processes of the textile factory SIMPO Dekor (Vranje, Serbia), and fly ash obtained from the power plant Nikola Tesla, Serbia.

To change the structural and surface properties of cotton and cotton/polyester yarns, two types of chemical modification were applied: modification with NaOH solution, and modification of cotton and cotton/polyester yarns with fly ash (FA) using sodium carboxymethyl cellulose (CMC) and sodium alginate (Al) as binders. Chemical modification with sodium hydroxide was carried on by immersing yarn samples in NaOH solution (10% and 18%), for one hour at room temperature. In the next step, the yarns were neutralized using 1 % acetic acid, washed with deionized water, and dried overnight at 60°C. Samples modified with 10% NaOH were denoted as P10 and P/PES10, and samples modified with 18% NaOH were denoted as P18 and P/PES18. Modification of cotton and cotton/polyester yarns with fly ash was performed through two cycles. In the first modification cycle, 0.1 g of material was weighed and immersed in 4 ml of a mixture of 0.5% binder solution and 0.1 g of fly ash for 10 minutes. Obtained materials were dried at 60 °C for 1 h. After drying, the second modification cycle was performed by re-immersing material in 4 ml of a mixture of a 0.5% binder solution and 0.1 g of fly ash for 10 minutes and afterward dried overnight at 60°C. Samples modified with fly ash using CMC as a binder were marked as P/CMC/FA and P/PES/CMC/FA, while samples obtained using Al as a binder were marked as P/Al/FA and P/PES/Al/FA.

2.2. Characterization of adsorbents

Scanning electron microscopy (SEM JEOL JSM-6610LV) was used to determine the morphological characteristics of unmodified and modified materials.

Fourier transform infrared spectroscopy (Nicolet™ iS™ 10 FT-IR Spectrometer, Thermo Fisher Scientific) was used to examine the content of functional groups on the material's surface.

The adsorption characteristics of the examined materials were tested through the adsorption of Cd and Pb from an aqueous solution. The unmodified and modified samples (0.02 g) were immersed in 20 cm^3 of an aqueous solution of Pb^{2+} or Cd^{2+} of the initial concentration 10 mg dm^{-3} in a batch system with constant mixing (150 rpm) for 3 hours. After the adsorption experiment, the metal concentration was measured by an atomic absorption spectrometer. Based on the obtained results, the removal efficiency of examined samples was calculated using the following equation:

$$RE = \frac{c_0 - c_e}{c_0} \cdot 100,\ \%$$

where c_e is the equilibrium and c_0 is the initial concentration of metal ions in solution (mg dm^{-3}).

3. RESULTS AND DISCUSSION

The structure and surface morphology of unmodified and modified cotton yarn samples are shown in Figure 1. Cotton fibers within the structure of unmodified yarns (Figure 1a) are spirally twisted and with a relatively smooth surface. Applied alkali treatment leads to increased surface roughness, featured by longitudinal cracks along the fiber, especially for the sample P18 (Figure 1c) where mercerization also induced higher liberation of cotton fibers in the yarn structure.

Figure 2 shows the morphology of unmodified and modified cotton/polyester yarn samples. The morphology of unmodified cotton-polyester yarns (Figure 2a), is characterized by the presence of cotton components and the presence of polyester fibers with a uniform tubular structure and smooth surface. It can be noticed that applied alkali treatment has no influence on the morphology of the polyester component (Figures 2b and 2c).

Figures 1d and 1e, and Figures 2d and 2e show the structure of cotton and cotton/polyester yarns combined with fly ash using alginate and CMC as binders, respectively. Fly ash is incorporated between cotton (Figures 1d and 1e), and cotton and polyester components (Figures 2d and 2e), and bound to them with an added binder.

Qualitative analysis of the functional groups present on the surface of unmodified and modified samples was analyzed by Fourier transform infrared spectroscopy. FTIR spectra for unmodified and alkali-modified cotton and cotton/polyester yarn samples are shown in Figure 3. The wide band between 3350 and 3250 cm^{-1} is assigned to the stretching vibrations of the O-H bond (hydroxyl groups), whereas the bands around 2920 and 2850 cm^{-1} are to be ascribed to asymmetric and symmetric C-H stretching vibrations, respectively. The broad peak around 1630 cm^{-1} can be attributed to the aromatic skeletal vibration or C=O stretching vibrations of carbonyl groups [18]. The bands in region 1150-1000 cm^{-1} are assigned to

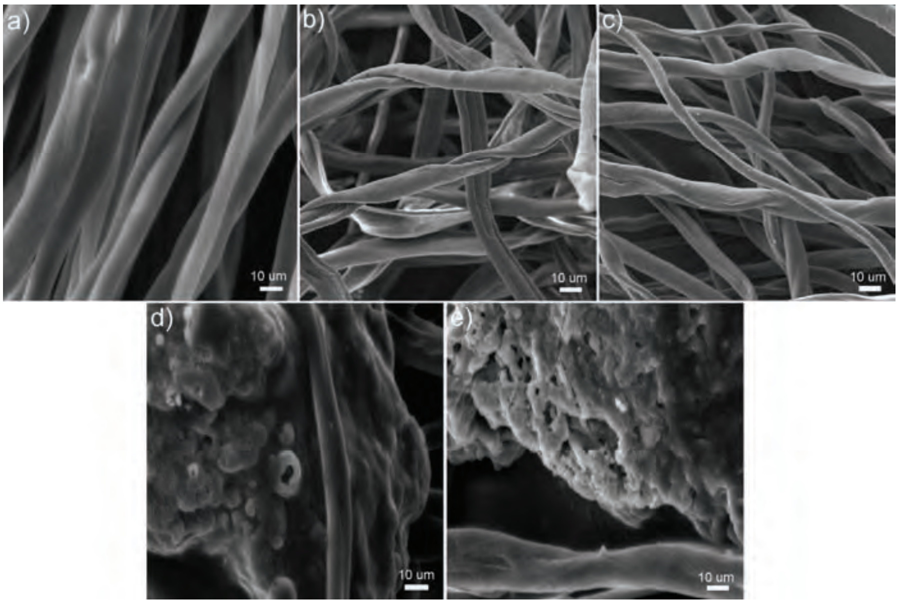

Figure 1: SEM photography of unmodified and modified cotton yarns:
a) P, b) P10, c) P18, d) P/Al/FA, and e) P/CMC/FA

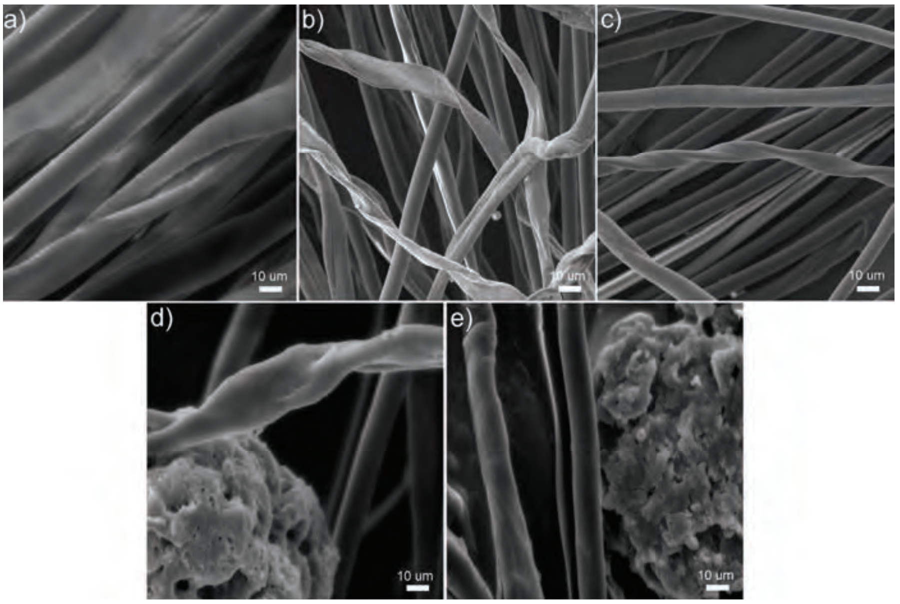

Figure 2: SEM photography of unmodified and modified cotton/polyester yarns:
a) P/PES, b) P/PES10, c) P/PES18, d) P/PES/Al/FA, and e) P/PES/CMC/FA

cellulose, indicating C-O and C-C stretching. Peaks at 1710 and 1240 cm^{-1} (Figure 3b) originated from the ester group, while peaks at 1505 cm^{-1} originated from aromatic systems in polyester chains [19].

Applied alkali treatment increased the availability of surface functional groups which is visible from the increase in the peak intensity of hydroxyl (bend in the range 3350-3250 cm^{-1}) and carbonyl (1240 cm^{-1}) groups. Also, absorption shoulders at 3487 cm^{-1} and 3444 cm^{-1} (Figure 3a), observed for sample P18, are characteristic for the general and specific O(3)H…O(5) intramolecular hydrogen-bonding of hydroxyl groups in cellulose II, respectively. This confirms that treatment with 18 % NaOH caused the polymorphic transformation of the origin cotton fibers crystal structure of cellulose (cellulose I) to more reactive cellulose II [20, 21]. Applied modification, and an increase in NaOH concentration, lead to the increase in the intensity of bands at 1710 and 1240 cm^{-1} (Figure 3b) and alter the surface chemistry of cotton components (changes in the region 1150-1000 cm^{-1}). Applied treatments induce the opening of the yarn structure, making ester groups more available.

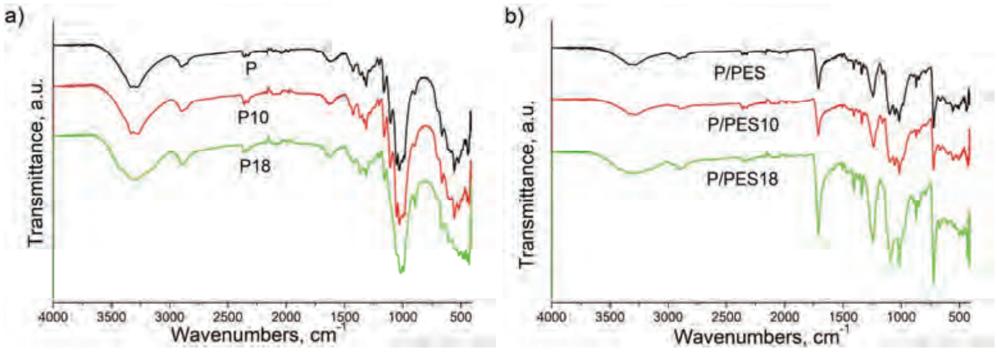

Figure 3: FTIR spectra of unmodified and alkali-modified a) cotton and b) cotton/polyester yarns

FTIR spectra of cotton and cotton/polyester yarns modified with fly ash in the presence of the binder, along with the FTIR spectra of FA, are shown in Figure 4. Compared to the FTIR spectra of unmodified P and P/PES samples, no additional bands are displayed on the FTIR spectra of samples modified with fly ash. A noticeable decrease in the intensity of the characteristic bands in the FTIR spectra of samples P/Al/FA and P/PES/Al/FA indicates that using alginate as a binder result in higher coverage of the surface of the yarns.

Unmodified and modified cotton and cotton/polyester yarns were used as adsorbents for lead and cadmium ions from the single-ion solutions. The efficiencies of the examined samples in removing the lead and cadmium ions from water are given in Figure 5. Unmodified cotton yarn shows slightly better lead and cadmium ions removal efficiency than unmodified cotton/polyester, due to the low adsorption capacity of a smooth and non-porous polyester component.

According to the results of characterization, applied alkali treatment leads to increased surface roughness, while mercerization induces higher liberation of cotton fibers and polymorphic transformation into more reactive cellulose II. Therefore, it could be expected that alkali treatment will have a positive effect on the adsorption properties of yarns.

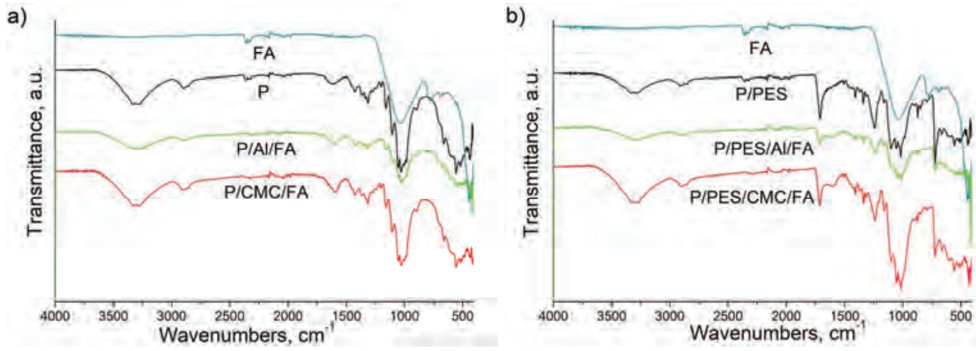

Figure 4: FTIR spectra of a) cotton and b) cotton/polyester yarns modified with fly ash

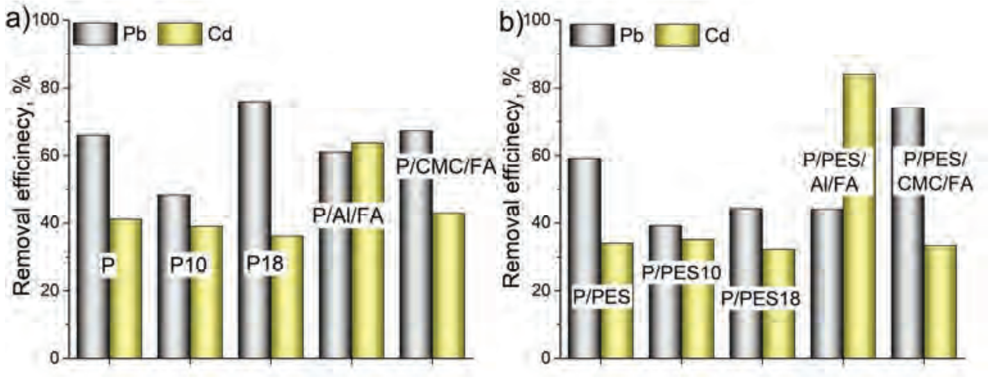

Figure 5: The removal efficiency of unmodified and modified
a) cotton and b) cotton/polyester yarns for the removal of lead and cadmium ions

However, applied alkali treatment only positively affects the adsorption properties of cotton yarns for lead ions removal, increasing the removal efficiency of P18 up to 75%.

Generally, examined yarn samples show higher efficiency in removing lead ions. The exceptions are the samples modified with fly ash using alginate as a binder since they show a higher ability to remove cadmium ions from water, with a removal efficiency of approximately 85% for sample P/PES/Al/FA.

Modification by the chemical coupling method has a higher impact on the adsorption characteristics of cotton polyester yarns due to the coverage of the polyester surface with binder and fly ash, which have a higher adsorption potential.

4. CONCLUSION

The impact of textile materials from production, consumption, and final disposal on the environment is the subject of extensive research nowadays. Fly ash is another industrial waste material generated in large quantities and requires safe disposal. One way to reduce the growing harmful effects of industrial waste is the use of environmentally and economically acceptable methods to convert these waste materials into adsorbents for wastewater treatment. In this study the effect of alkalization and chemical coupling methods on the surface and adsorption properties on two kinds of waste materials, cotton and cotton/polyester yarns and fly ash was investigated. Applied alkali modification, and an increase in NaOH concentration, alter the structure and surface chemistry of cotton yarns and induce the opening of the yarn structure. This treatment also makes ester groups in the polyester component in cotton/polyester yarns more available. However, this method of modification positively affected only the adsorption properties of cotton yarns for lead ions removal, increasing the removal efficiency to 75%. The chemical coupling method of modification had a greater impact on the adsorption properties of cotton polyester yarns, where the covering of polyester fibers with fly ash and binder contributes to the increase in the number of active sites for binding metal ions. The relatively high removal efficiencies obtained for lead ions on P/PES/CMC/FA (77%) and cadmium on P/PES/Al/FA (85%) indicate that these materials can be used as adsorbents for heavy metals removal from water. Thus, the successful reuse of waste materials was carried out, and at the same time, the goals of sustainable development, circular economy, and environmental protection were achieved.

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