MODIFIED FIBROUS TEXTILE WASTE AS ADSORBENTS FOR REMOVAL OF PHARMACEUTICALS FROM WATER

Original scientific paper
DOI:10.5937/CT_ITI24008V

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ABSTRACT: *Textile industry is a significant environmental polluter, generating vast amounts of waste during production, processing, dyeing, and distribution. Disposing of chemical and solid textile waste poses serious risks to soil, water, and air quality. In order to mitigate this inconvenience, solid textile waste can be reused through redesign or recycling methods. One such method involves repurposing textile waste as adsorbent or as a raw material for carbon adsorbent preparation. In this study, fibrous textile waste, waste cotton yarns and flax fibers were utilized as cost-effective resources for carbon material production. Carbon materials were derived from waste fibers and yarns through carbonization and subsequent activation using KOH as an activating agent. The adsorption characteristics of newly prepared materials were examined through the adsorption of various drugs from water. Factors such as contact time, initial concentration, and pH of the drug mixture in an aqueous solution were studied to understand their impact on the adsorption capacity of carbon adsorbents. The obtained results were analyzed using pseudo-first and pseudo-second order kinetics models, Freundlich and Langmuir isotherms. It has been shown that carbon materials obtained by the activation of cotton yarn and flax fibers can be used as highly efficient adsorbents for the rapid removal of drugs from water.*

Keywords: *cotton yarn, flax fibers, textile waste, adsorption, pharmaceuticals.*

ADSORPCIJA LEKOVA IZ VODE PRIMENOM MODIFIKOVANOG VLAKNASTOG TEKSTILNOG OTPADA

APSTRAKT: *Tekstilna industrija je jedan od najvećih zagađivača životne sredine zbog ogromnih količina otpada koji se generišu tokom proizvodnje, obrade, bojenja i distribucije. Odlaganje hemijskog i čvrstog tekstilnog otpada nosi ozbiljne rizike po kvalitet zemljišta, vode i vazduha. Da bi se ublažio negativni uticaj tekstilne industrije na životnu sredinu, čvrsti tekstilni otpad se može ponovo upotrebiti korišćenjem metoda redizajniranja ili recikliranja. Jedan od vidova ponovne upotrebe tekstilnog otpada je njegovo korišćenje kao adsorbenta ili sirovine za proizvodnju ugljeničnih adsorbenata. U cilju smanjenja količine vlaknastog tekstilnog otpada, u ovom radu je ispitana mogućnost njegovog korišćenja za dobijanje ugljeničnih adsorbenata. Primenom metoda karbonizacije i naknadne aktivacije u prisustvu KOH kao aktivirajućeg agensa, polazeći od pamučnog prediva i vlakana lana dobijeni su ugljenični materijali. Adsorpcione karakteristike dobijenih materijala ispitivane su adsorpcijom ostataka kardiovaskularnih lekova iz vode. Ispitan je uticaj vremena kontakta, početne koncentracije i početne pH vrednosti smeše lekova na adsorpcioni kapacitet pripremljenih adsorbenata. Dobijeni rezultati su analizirani korišćenjem kinetičkih modela pseudo-prvog i pseudo-drugog reda, kao i Frojndlihove i Lengmirove adsorpcione izoterme. Pokazano je da se karbonizacijom i naknadnom aktivacijom pamučnog prediva i vlakana lana mogu dobiti visoko efikasni adsorbenti za brzo uklanjanje lekova iz vode.*

Ključne reči: *pamučno predivo, vlakna lana, tekstilni otpad, adsorpcija, lekovi.*

1. INTRODUCTION

The textile industry generates vast quantities of waste, much of which ends up in landfills or incinerators, contributing to soil, water, and air pollution. However, recent research has explored innovative approaches to repurpose textile waste, offering potential solutions to both environmental and economic concerns. One promising avenue is the thermal modification of textile waste, particularly through processes like carbonization and chemical activation [1,2]. Carbonization involves subjecting organic materials to high temperatures in an inert atmosphere, resulting in the conversion of these materials into carbonaceous residues. On the other hand, chemical activation involves treating carbonized materials with activating agents to create a porous structure, enhancing their adsorption properties. Cotton yarn and flax fibers, which are part of solid textile waste, are rich in cellulose and lignocellulosic components and exhibit considerable potential for transformation into effective adsorbents through thermal modification processes [3,4]. The resulting carbon-based adsorbents retain the fibrous structure of the original textile waste while offering enhanced surface area and porosity, ideal for adsorption applications [5].
In this work, we focus on the application of cotton and flax fibers-based carbon adsorbents for the purification of water contaminated with pharmaceuticals from the class of cardiovascular (enalapril, cilazapril, metoprolol, clopidogrel). Pharmaceuticals, emerging

as significant contaminants in water sources due to their widespread use and incomplete removal by conventional wastewater treatment processes, pose risks to human health and ecosystems [6]. The utilization of modified fibrous textile waste as adsorbents for pharmaceutical removal offers several advantages. Firstly, it provides a sustainable solution to both the textile waste problem and water contamination, aligning with principles of circular economy and environmental management. Additionally, the fibrous nature of the adsorbents facilitates the filtration of water, allowing efficient removal of different pollutants. Through systematic experimentation, we explore the adsorption capacity, kinetics, and mechanisms of cotton and flax fibers-based carbon adsorbents towards various pharmaceutical compounds commonly found in water sources.
Overall, this paper contributes to the growing body of research on sustainable materials and technologies for water purification, demonstrating the potential of thermally modified fibrous textile waste as an effective adsorbent for the removal of pharmaceuticals from water.

2. MATERIALS AND METHODS

Waste cotton yarn and flax fibers were used as a starting material for obtaining carbon adsorbents in the process of carbonization, followed by chemical activation. Carbonization was performed in an electrical furnace in an inert nitrogen atmosphere at 900 °C, with a heating rate of 5 °C/min. After carbonization, the obtained materials were activated in the presence of KOH, as an activating agent, where the mass ratio of KOH and carbonized material was 1:2. Activation was also performed in an inert nitrogen atmosphere at a temperature of 900 °C, with a heating rate of 5 °C/min. Activated carbon material obtained from cotton yarn was labeled as AcC, while the activated sample obtained from flax fibers was labeled as AcF.
Adsorption experiments were performed in a batch system, with constant mixing (150 rpm). For adsorption efficiency examination, 0.02 g of carbon sample was immersed in 25 cm^3 of a mixture of selected pharmaceuticals with an initial concentration of 1 mg/dm^3 of each analyte. The influence of the initial pH of the solution on the adsorption efficiency of activated carbon samples was examined by adjusting the initial pH to values of 2, 4, 6, 8, and 10. The influence of contact time was examined by the adsorption of pharmaceuticals from 50 cm^3 of solution (2.5 mg/dm^3) onto 0.1 g AcC and AcF. At certain time intervals (10, 15, 30, 60, 120, and 180 minutes) samples were taken, and the pharmaceutical concentration was determined by liquid chromatography-tandem mass spectrometry. The experimental data were analyzed using the pseudo-first (Eq. 1) and the pseudo-second order model (Eq. 2):

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

$$q_t = q_e - \left(\frac{1}{q_e} + k_2 t\right)^{-1} \quad (2)$$

where q_e (mg/g) is the equilibrium adsorbed amount of adsorbate per unit mass of adsorbent, q_t (mg/g) is the amount of adsorbate per unit mass of adsorbent in time t (min), k_1 (1/min), and k_2 (g/(mg min)) are the pseudo-first, and the pseudo-second order rate constants.

The influence of initial adsorbate concentration on adsorption was examined through the adsorption of cardiovascular pharmaceutical (25 cm^3, initial concentration of 1.5; 2.5; 3.5, and 5 mg/dm^3) onto 0.02 g AcC and AcF. Collected data were fitted with Langmuir (Eq. 3) and Freundlich (Eq. 4) adsorption isotherm:

$$q_e = \frac{Q_0 b C_e}{1+C_e} \quad (3)$$

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

where C_e (mg/dm^3) is the equilibrium concentration of adsorbate in the solution, Q_0 (mg/g) is the maximum adsorption capacity, b (dm^3/mg) is the Langmuir constant, and K_f ($mg^{1-1/n}dm^{3/n}g^{-1}$) and $1/n$ are empirical Freundlich constants.

3. RESULTS AND DISCUSSION

The pH value of a pharmaceutical solution is a significant factor, which can affect the adsorption efficiency of examined adsorbents. The influence of the initial pH value on the adsorption efficiency of AcF and AcC is given in Figure 1.

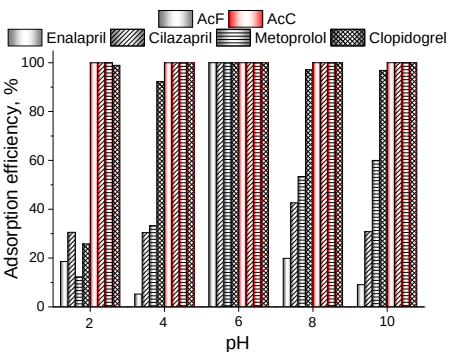

Figure 1: The influence of initial pH value on the adsorption efficiency of AcF and AcC toward cardiovascular drugs

The adsorption efficiency of AcC does not depend on the initial pH value, since this sample completely removed all examined cardiovascular drugs from the water solution. On the other hand, adsorption onto AcF is influenced by initial pH and depends on the polarity of the pharmaceutical; generaly the highest adsorption efficiency is obtained for less polar compounds. The highest adsorption efficiency for both samples is observed for an initial pH value of 6, and therefore this value is taken as an optimal pH for the following adsorption experiments.

The influence of contact time on the adsorption capacities of AcC and AcF is shown in Figure 2, along with the fitting of experimental data with pseudo-first and pseudo-second kinetic models. Kinetic parameters obtained by fitting of experimental data with kinetic models are presented in Table 1.

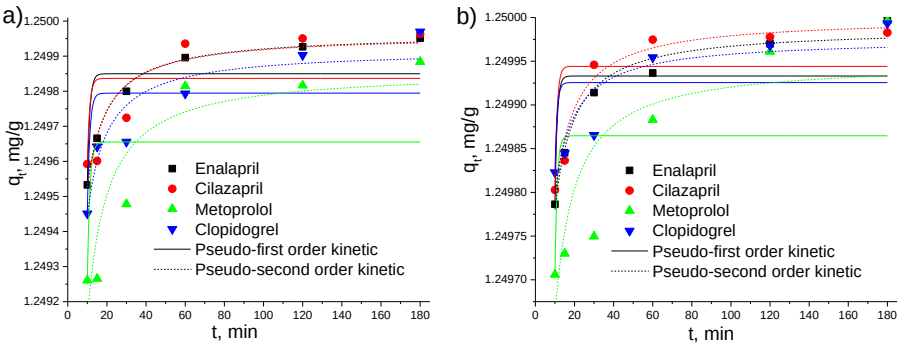

Figure 2: The influence of contact time on adsorption capacities of a) AcF and b) AcC

Table 1: Kinetic parameters for adsorption of cardiovascular drugs onto AcF and AcC

Sample	Analyte	Pseudo-first order			Pseudo-second order			$q_{e,exp}$, mg/g
		$q_{e,cal}$, mg/g	k_1, 1/min	R^2	$q_{e,cal}$, mg/g	k_2, g/(mg min)	R^2	
AcF	Enalapril	1.2499	0.8267	0.51888	1.2500	227.3	0.99477	1.2500
	Cilazapril	1.2498	0.8521	0.15617	1.2500	229.3	0.82950	1.2500
	Metoprolol	1.2497	0.8035	0.15089	1.2499	140.7	0.82649	1.2499
	Clopidogrel	1.2498	0.8189	0.42879	1.2499	209.6	0.85390	1.2500
AcC	Enalapril	1.2499	0.9040	0.47312	1.2500	481.6	0.96942	1.2500
	Cilazapril	1.2499	0.9076	0.41363	1.2500	481.1	0.95587	1.2500
	Metoprolol	1.2499	0.8957	0.08645	1.2500	343.2	0.69924	1.2500
	Clopidogrel	1.2499	0.9396	0.17587	1.2500	569.2	0.79681	1.2500

The adsorption capacities of both samples increase with time, with very fast initial adsorption. Already after 10 minutes, the adsorption process reaches equilibrium, and both samples almost completely remove the drugs from the solution. According to the correlation coefficients (R^2) and the equilibrium adsorption capacities calculated by the models used (Table 1), the adsorption of cardiovascular drugs onto AcF and AcC can be described by pseudo-second order kinetic model.

Although adsorption capacity increases with the initial concentration, there is no characteristic plot on the q_e-C_e dependence (Figure 3), which indicates the lack of surface saturation in an examined concentration range, especially in the case of clopidogrel adsorption on both adsorbents.

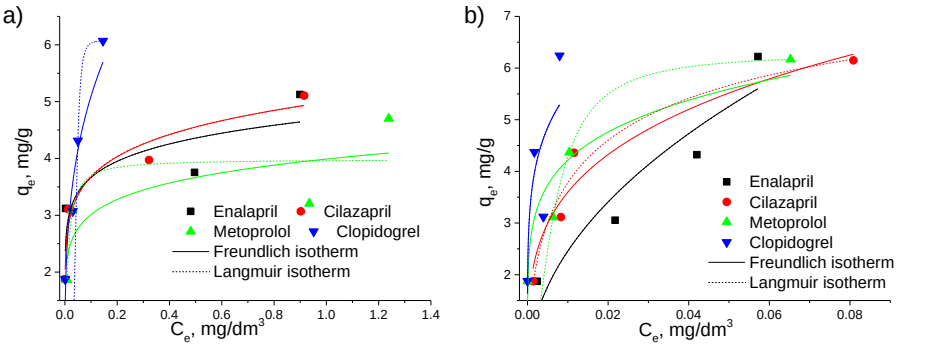

Figure 3: Influence of initial concentration on a) AcF and b) AcC adsorption capacities and fitting of equilibrium data with Langmuir and Freundlich isotherm model

Adsorption equilibrium data were fitted with Langmuir and Freundlich isotherm models and the obtained parameters are summarized in Table 2.

Table 2: Isotherm parameters for adsorption of cardiovascular drugs onto AcF and AcC

Sample	Analyte	Freundlich isotherm			Langmuir isotherm		
		K_f, $mg^{1-1/n}dm^{3/n}g^{-1}$	1/n	R^2	Q_0, mg/g	b, dm^3/mg	R^2
AcF	Enalapril	4.70	0.108	0.66354	316.75	0.015	0.32670
	Cilazapril	4.99	0.133	0.92789	73.81	0.072	0.85560
	Metoprolol	3.99	0.122	0.51341	3.99	146.8	0.17959
	Clopidogrel	10.06	0.295	0.80297	2340.67	0.004	0.79029
AcC	Enalapril	21.66	0.473	0.81483	3312.12	0.01	0.62929
	Cilazapril	12.23	0.266	0.91694	8.88	8.79	0.88768
	Metoprolol	9.46	0.175	0.84750	6.29	5720.48	0.04571
	Clopidogrel	13.07	0.187	0.50483	1719.64	0.01	0.00933

According to the correlation coefficients (R^2) Freundlich adsorption isotherm better describes the adsorption of cardiovascular drugs onto both adsorbents. The highest maximal adsorption capacities (Q_0) are obtained for the adsorption of clopidogrel on AcF and enalapril on AcC. For both adsorbents, obtained heterogeneity factor (1/n) values are close to 0, implying that the surfaces of examined materials are relatively heterogeneous and that the adsorption of selected pharmaceuticals is most likely a chemical process.

3. CONCLUSION

The current study underscores the utilization of fibrous textile waste as a primary material for the production of effective carbon adsorbents. By employing waste flax fibers and cotton yarn and subjecting them to carbonization followed by the activation processes, we successfully developed two highly efficient adsorbents capable of removing cardiovascular

drugs from water. Our findings demonstrate that the adsorption of selected pharmaceuticals onto activated flax fibers is dependent on the initial pH value. Moreover, less polar compounds exhibit a greater affinity towards this adsorbent. Conversely, activated cotton yarn demonstrates consistent and nearly complete removal of selected drugs regardless of the initial pH value of the solution. Furthermore, the adsorption of cardiovascular drugs was observed to be a rapid process, conforming to the pseudo-second order kinetic model, while equilibrium adsorption, can be aptly described by the Freundlich isotherm model. These results conclusively indicate that the waste flax fibers and cotton yarn can be effectively reused for the production of highly efficient carbon adsorbents, facilitating the rapid removal of cardiovascular drugs from water.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-65/2024-03/200135, 451-03-66/2024-03/200287 and 451-03-66/2024-03/200017).

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