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EFFECT OF COIR CHEMICAL MODIFICATION ON THEIR SORPTION OF SELECTED HEAVY METALS

WPLYW MODYFIKACJI CHEMICZNEJ WŁÓKNA KOKOSOWEGO NA ZDOLNOŚĆ SORPCYJNĄ WYBRANYCH METALI CIĘŻKICH

Abstract: The paper presents the results of removal of heavy metals ions from aqueous solution by adsorption. Zn(II), Cd(II), Co(II), Cu(II) and Ni(II) were adsorbed on lignocellulosic sorbent, a natural polymer (concentration range: 20–50 mg/dm³). Sorption capacity was determined for raw and chemically modified coir fibres. Fibre samples activated with 30 % H₂O₂ solution and 5 % NaOH solution were tested. Fibres modified with sodium hydroxide were found to have the highest sorption capacity. Samples treated with H₂O₂ were found the least effectiveness. The results showed that the time required to reach equilibrium for most of the metal ions was approximately 5 hours. The equilibrium sorption data for test ions were analyzed using three widely applied isotherms: Redlich–Peterson, Freundlich and Langmuir. Assessment of statistical parameters confirmed that a good fit to experimental data for most of cases was obtained. The test results confirmed that coir is an efficient sorbent for the removal of heavy metals ions from water and that it may be used as an alternative biosorbent for the treatment of contaminated water.

Keywords: coir, chemical modification, sorption equilibrium, heavy metal ions

Introduction

Regions dominated by industry with large mining, metallurgy and galvanizing plants are the main sources of heavy metals emission and environment contamination. Heavy metals are characterized by high toxicity and persistence in the environment due to the ability to change their chemical structure *ie* type of chemical bonds. Chemical bonds between certain metals result in environment exposure to a whole group of these elements: *eg* zinc ores often contain lead, copper and cadmium [1, 2].

Water is one of the prime elements responsible for life on earth so the biggest threat are compounds with good water solubility that easily pass through barriers such as cell walls, damaging them as they migrate. The amount of metals that may be dissolved in a solution depends on its reaction, presence of other substances, concentration of anions and organic and inorganic chelating ligands [3].

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Many authors stress that increasing level of heavy metals in different components of the environment is a global problem [4, 5]. At present it is difficult to define the risk quantitatively as there is no data concerning risk identification and assessment, and information on the impact of individual elements is fragmentary.

Application of cost-intensive methods of heavy metals separation has led to the search for available and renewable ion exchange materials. Novel studies are designed to investigate unconventional plant/natural lignocellulosic products and adsorbents such as: corncobs [6], banana fibers [7], scobs [8], chitosan [9] or buckwheat hull [10].

Materials and method

The aim of the study was to evaluate the process of heavy metals sorption onto fibrous coir as an alternative method of water treatment, allowing for the removal of harmful contaminants. The studies were performed using a raw and chemically modified sorbent. The results have been analyzed by most commonly used Langmuir, Freundlich and Redlich–Peterson isotherms.

Materials

Coir is one of the environment-friendly sorbents that is a by-product of coconut processing. Fibrous mass is extracted from the outer shell of a coconut (*Cocos nucifera*). The palm is grown in all tropical regions, but most of the fibers used in the industry have their origin in India and Sri Lanka. The plant is grown for food.

Coir is a hygroscopic material, highly resistant to abrasion, harsh weather conditions and salt water. It is made of fibrous bundles of 10–35 cm in length and 12–25 μm in diameter. The fiber is composed of cellulose (ca 28 %), hemicellulose polysaccharides (38 %) and lignin (35 %) that makes the material strong and stiff [11]. The fibers are able to complex and adsorb metals as a result of ion exchange and chemical processes, which makes them a cost effective adsorbent and allows for the use of waste materials obtained as a result of the plant material processing.

Raw coir was boiled at 90 °C and washed with distilled water to remove dirt. Then the fibers were cut to obtain 3–5 cm long fibers and modified chemically:

- K1 – fibers boiled at 90 °C,
- K2 – fibers boiled at 90 °C + 30 % H_2O_2 ($t = 3$ h, $T = 25$ °C),
- K3 – fibers boiled at 90 °C + 30 % H_2O_2 ($t = 3$ h, $T = 90$ °C),
- K4 – fibers boiled at 90 °C + 5 % NaOH ($t = 3$ h, $T = 25$ °C),

The obtained fibrous samples were washed with distilled water and dried until solid mass was obtained.

Experimental

Five batches of aqueous solutions were prepared of specific analyte concentration (10–50 mg/dm^3) and uniform composition (ZnSO_4 , CdSO_4 , CoSO_4 , CuSO_4 , NiSO_4) – Fluka, Germany. In a multicomponent solution concentration of each component of the mixture was the same, which means that each of the cations in the solution was

concentrated *eg* 50 mg/dm³. Samples of coir (5 g) were placed into conical flasks and 200 cm³ of test solution was added (pH = 5). The mixture was then mechanically shaken on a water bath until adsorption equilibrium was achieved ($T = 25\text{ }^{\circ}\text{C}$). Heavy metals concentration was determined by IC (ICS-1000, IonPac AS5A, Dionex).

Mathematical description of equilibrium

Based on the initial C_0 [mg/dm³] and current concentration C_t [mg/dm³] in the analyzed systems, the sorption capacity of adsorbed ions was calculated using the following formula (1):

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

where: q – sorption capacity [mg/g],
 C_0 – initial concentration of heavy metal ions [mg /dm³],
 C_t – concentration of heavy metal ions after time t [mg/dm³],
 m – mass of adsorbent [g],
 V – solution volume [dm³].

Langmuir, Freundlich and Redlich–Peterson classic sorption formulas were used to analyze the equilibrium experiment.

Adsorption isotherm was developed by Langmuir in 1916. It owes its popularity to a relatively simple form and satisfactory conformity of experimental and theoretical values.

$$\frac{q_e}{q_m} = \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

where: q_e – equilibrium ion concentration in the sorbent [mg/g d.m. coir],
 C_e – equilibrium ion concentration in the solution [mg/dm³],
 K_L, q_m – Langmuir constants describing sorption equilibrium.

As stated in the monolayer adsorption theory, adsorption equilibrium in the solid-liquid system may be described by an empirical equation called Freundlich isotherm.

$$q_e = K_F \cdot C_e^n \quad (3)$$

K_F, n – Freundlich constants describing sorption equilibrium.

Redlich–Peterson model was developed as a result of compilation of Langmuir and Freundlich equations. The above relationships is in the following form:

$$q_e = \frac{K_{RP} \cdot C_e}{1 + B \cdot C_e^a} \quad (4)$$

K_{RP}, B, a – Redlich–Peterson constants describing sorption equilibrium.

Results and discussion

The results of experiments and calculations are presented in the Figures below. Figures 1 and 2 present the concentration profile change for Cu(II) and Cd(II) ions as a function of time. In both cases, best results of metal recovery were obtained for samples modified with 5 % NaOH (K4). Raw fibers (K1) had smaller sorption capacity. In the case of the two other modifications (K2 and K3) lower values of adsorbed ions were obtained, even compared with unmodified material.

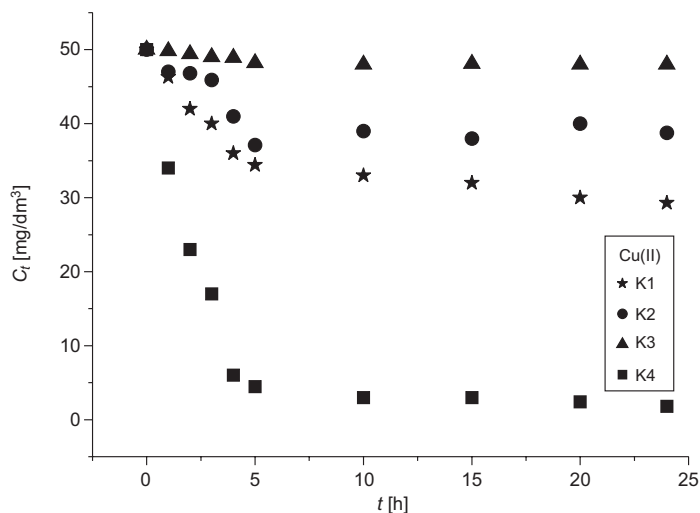


Fig. 1. Adsorption kinetics of Cu(II) onto coir K1, K2, K3, K4 ($C_0 = 50 \text{ mg/dm}^3$)

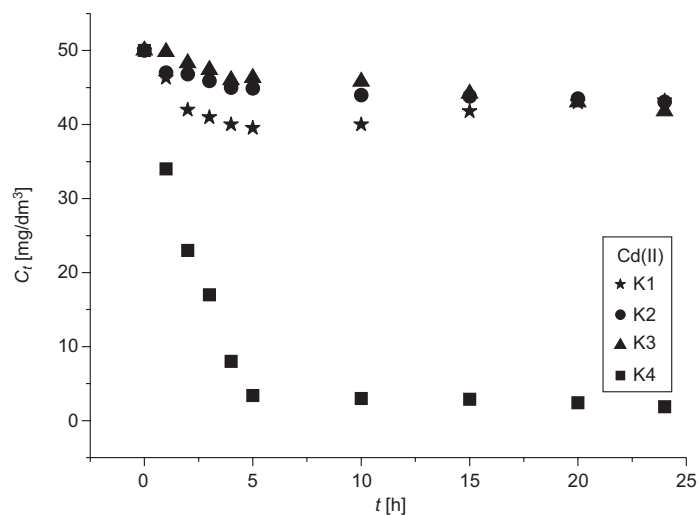


Fig. 2. Adsorption kinetics of Cd(II) onto coir K1, K2, K3, K4 ($C_0 = 50 \text{ mg/dm}^3$)

This was probably due to too aggressive chemical modification with an oxidant (H_2O_2) and high temperature. A similar tendency was also observed for Zn(II), Ni(II) and Co(II) ions within the whole range of analyzed concentrations.

Therefore, further experiments were carried out for K1 and K4 fibers. K4 material showed a comparable adsorption capacity for all of the analyzed metals ($q_{\text{Cu}} = 1.93$ mg/g, $q_{\text{Ni}} = 1.91$ mg/g, $q_{\text{Zn}} = 1.92$ mg/g, $q_{\text{Co}} = 1.89$ mg/g, $q_{\text{Cd}} = 1.93$ mg/g).

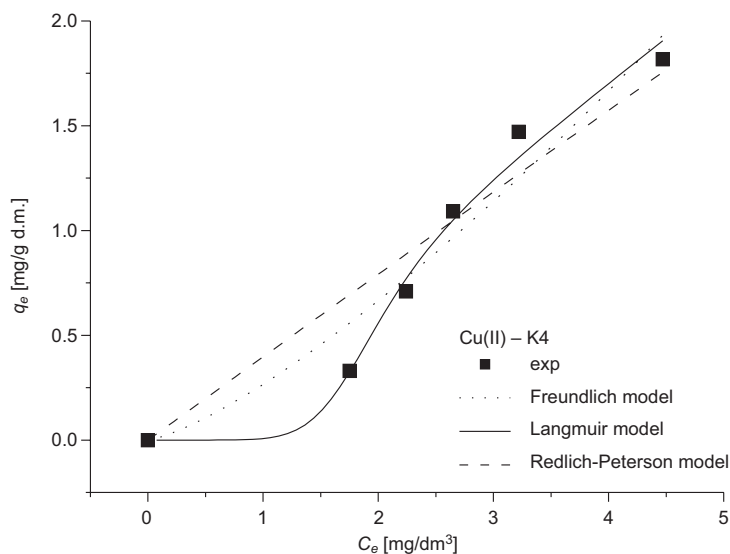


Fig. 3. Redlich–Peterson, Langmuir and Freundlich isotherms for Cu(II) sorption onto K4

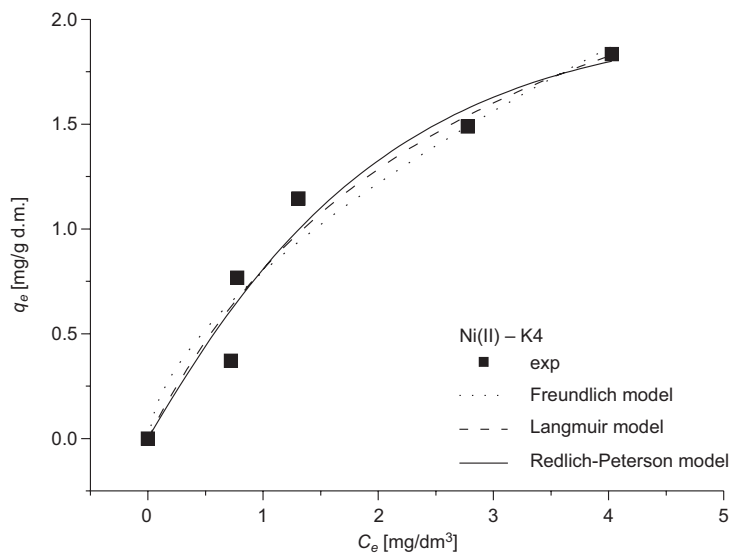


Fig. 4. Redlich–Peterson, Langmuir and Freundlich isotherms for Ni(II) sorption onto K4

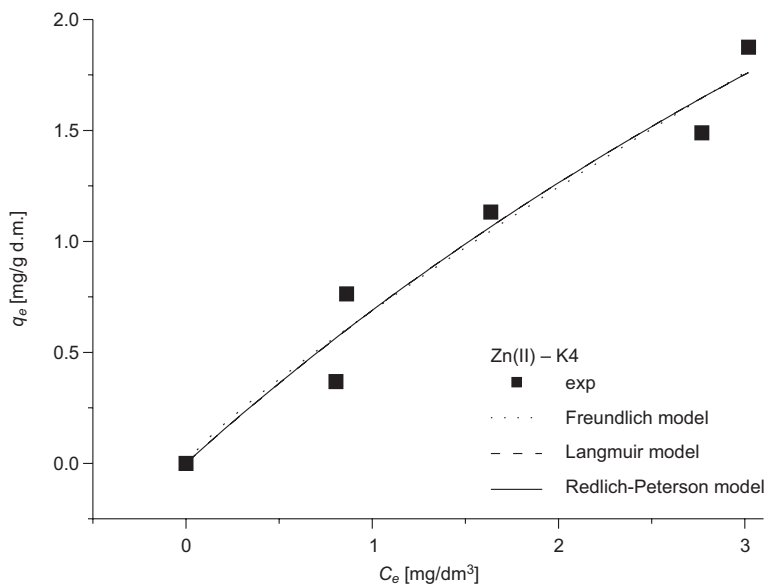


Fig. 5. Redlich–Peterson, Langmuir and Freundlich isotherms for Zn(II) sorption onto K4

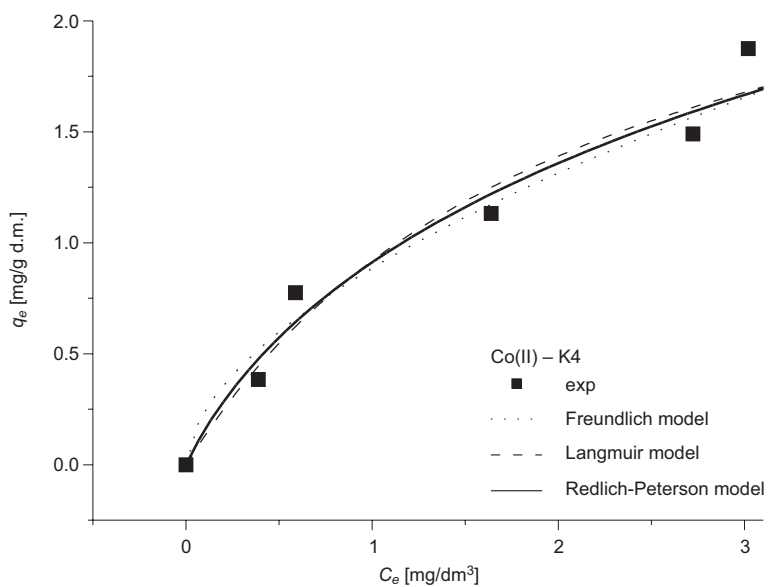


Fig. 6. Redlich–Peterson, Langmuir and Freundlich isotherms for Co(II) sorption onto K4

Characteristics parameters for the discussed models are presented in Table 1. The sorption isotherm models showed the square determination coefficient of $R^2 = 0.912\text{--}0.988$, which confirms that sorption models are well suited to analyze experimental data.

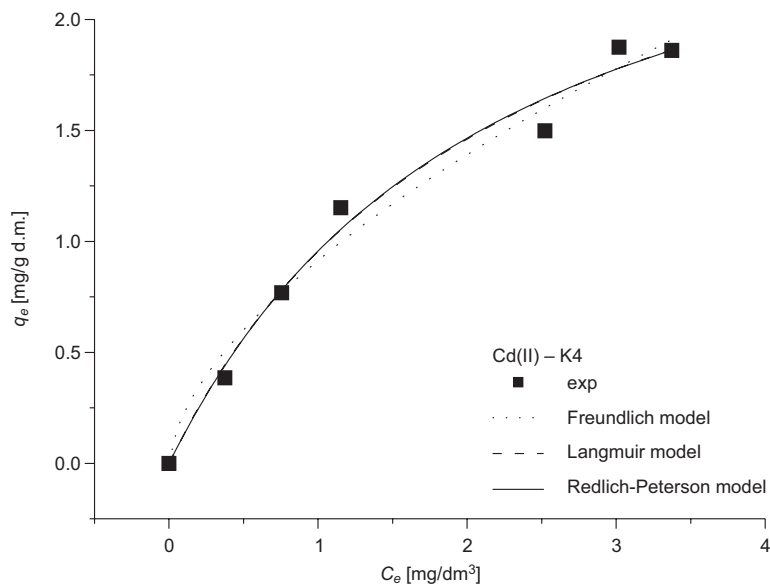


Fig. 7. Redlich–Peterson, Langmuir and Freundlich isotherms for Cd(II) sorption onto K4

As stated above, lower adsorption values were obtained with K1 material. Raw fibers had the highest sorption capacity toward copper ions ($q_{Cu} = 1.38$ mg/g) and showed the lowest affinity for cobalt ($q_{Co} = 0.15$ mg/g).

Table 1

Specification of Redlich–Peterson, Langmuir and Freundlich models for coir K4

Model	Parameter	Cu	Ni	Zn	Co	Cd
Freundlich	K_F [mg/g] [dm^3/mg] ^{1/n}	0.266	0.796	0.687	0.886	0.914
	n	1.323	0.613	0.857	0.568	0.605
	R^2	0.944	0.945	0.956	0.969	0.981
Langmuir	q_m [mg/g]	117.6	3.14	7.683	2.857	3.109
	K_L [dm^3/mg]	0.003	0.347	0.099	0.474	0.444
	R^2	0.912	0.955	0.956	0.970	0.986
Redlich–Peterson	K_{RP} [dm^3/g]	58.06	0.154	0.105	1.032	0.411
	a [dm^3/mg] ^{1/n}	−6.78	1.405	0.969	0.743	1.036
	B	0.007	6.076	7.288	1.796	3.288
	R^2	0.988	0.957	0.956	0.972	0.986

Chemical modification with H_2O_2 (K2) significantly reduced sorption capacity toward all ions as shown in Figures 8 and 9. The application of hydrogen peroxide as a modifying factor resulted in significantly lower sorption capacity.

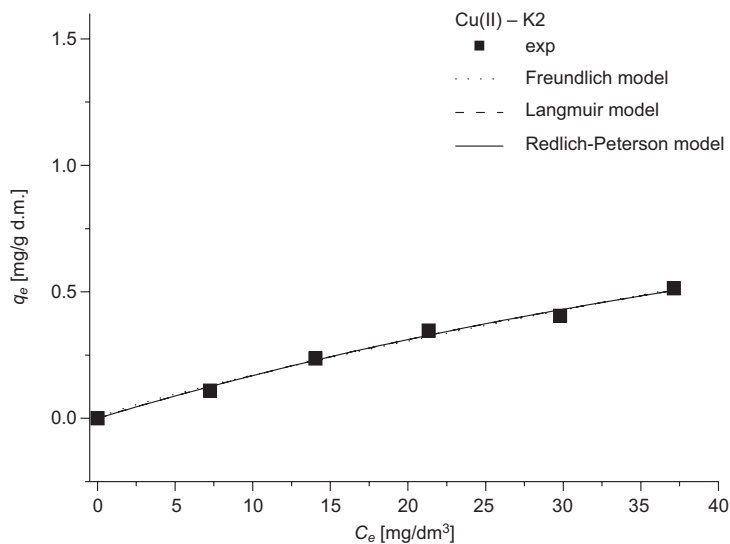


Fig. 8. Redlich–Peterson, Langmuir and Freundlich isotherms for Cu(II) sorption onto K2

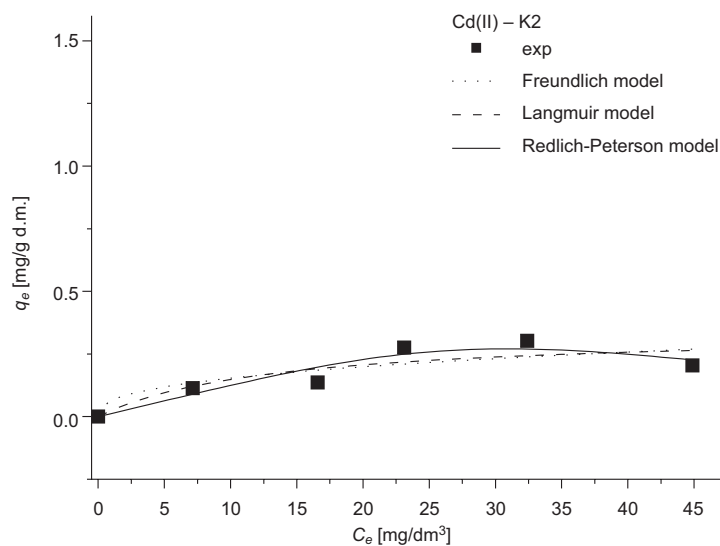


Fig. 9. Redlich–Peterson, Langmuir and Freundlich isotherms for Cd(II) sorption onto K2

Conclusions

1. Four methods of coir modification were tested. It was expected that modification with H_2O_2 and NaOH would improve sorption capacity. The results shown that only

modification with 5 % NaOH improved sorption capacity. Affinity for heavy metals sorption on K4 fiber was much higher than for other materials used in the experiment. Fibers modified with H₂O₂ had the lowest, and indeed very small, sorption capacity.

2. It was shown however, that accordingly modified coir is an effective material for the removal of heavy metals from aqueous solutions and it may serve as an alternative to more expensive, conventional adsorbents.

3. Sorption capacity of a given material depends on modification method. Additionally, it may be assumed that adsorbate location and transfer mechanism may be dependent on the number of mixture components *ie* ion competitiveness in binding to the active sites.

4. Langmuir, Freundlich and Redlich–Peterson models described the experimental data well within the whole range of analyzed concentrations.

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WPLYW MODYFIKACJI CHEMICZNEJ WŁÓKNA KOKOSOWEGO NA ZDOLNOŚĆ SORPCYJNĄ WYBRANYCH METALI CIĘŻKICH

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Abstrakt: W pracy zaprezentowano wyniki badań adsorpcyjnego usuwania jonów metali ciężkich z roztworu wodnego. Adsorpcja Zn(II), Cd(II), Co(II), Cu (II) oraz Ni (II) była prowadzona na roślinnym sorbencie – włóknach orzecha kokosowego (zakres stężeń 20–50 mg/dm³). Określono wydajność sorpcyjną dla surowych i modyfikowanych chemicznie włókien. Włókna aktywowano 30 % roztworem H₂O₂ oraz 5 % roztworem NaOH. Najwyższą pojemność sorpcyjną wykazały włókna modyfikowane NaOH, zaś najmniejszą traktowane H₂O₂. Równowagę procesu adsorpcji dla większości jonów metali osiągnięto po około 5 h. Do opisu równowagi sorpcji badanych jonów przetestowano trzy równania: Redlicha–Petersona, Freundlicha i Langmuira.

Analiza parametrów oceny statystycznej potwierdziła, że we wszystkich przypadkach uzyskano dobre dopasowanie do danych eksperymentalnych. Uzyskane wyniki badań potwierdzają użyteczność włókna kokosowego w procesie usuwania metali ciężkich z wody oraz jego przydatność jako alternatywnego biosorbentu uzdatniającego wodę.

Słowa kluczowe: włókno kokosowe, modyfikacja chemiczna, równowaga sorpcyjna, metale ciężkie