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[Marin Nicoleta](#)*

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Article

Green Chemistry Applications Using Complexing Materials for Metal Ions Removal from Aqueous Media

Nicoleta Mirela Marin ^{1,2,3}

¹ National Research and Development Institute for Industrial Ecology ECOIND, Street Podu Dambovitiei no. 57-73, District 6, 060652 Bucharest, Romania

² Department of Oxide Materials Science and Engineering, National University of Science and Technology Politehnica Bucharest, 1–7 Gh. Polizu, 060042 Bucharest, Romania

³ Department of Analytical and Physical Chemistry, University of Bucharest, 4-12 Regina Elisabeta Bd., 030018 Bucharest, Romania

* Correspondence: nicoleta.marin@incdecoind.ro

Abstract: In this study two complexing materials were obtained for Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} removal from aqueous media. Synthetic cellulose powder (CELL) and cellulosic green material obtained from shredded maize stalk (MS) were modified with direct red 23 (DR 23) a complexing agent. Chelating materials MS-DR 23 and CELL-DR 23 were obtained by batch mode technique. Experimental parameters like interaction time, pH of aqueous solution, and initial concentration of DR 23 were studied to optimized the complexing process. The time necessary to reach equilibrium was 75 min for both cellulose materials. Also, pH=2 was the optimum adsorption value for DR 23 adsorption. The adsorption capacity for MS (56.8 mg/g) was more significant than for CELL (42 mg/g). Applicability of complexing materials was checking for Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} (M^{x+}) removal. The concentration of M^{x+} retained on cellulosic materials was detected by AAS method. The formation of complex between DR 23 and M^{x+} was evaluated across different pH levels: 2.0, 4.0, 6.0, 8.0 and 10.0. Batch adsorption experiments were conducted to assess the adsorption of M^{x+} onto MS-DR 23 and CELL-DR 23. The optimum contact time for evaluating metal adsorption was established at 90 min. A high level of metal adsorption was reported at 4 mg/L. The maximum adsorption capacity for MS-DR 23 was found to be 1.32 mg/g Mn^{2+} , 1.30 mg/g Zn^{2+} , 1.26 mg/g Fe^{3+} and 1.20 mg/g Cr^{3+} , while for CELL-DR 23 it was 1.21 mg/g Mn^{2+} , 1.08 mg/g Zn^{2+} , 1.23 mg/g Fe^{3+} and 1.0 mg/g Cr^{3+} . Reusability experiments conducted with 0.5 M HCL solution demonstrated effective regeneration and reusability of MS-DR 23 and CELL-DR 23, this suggests that MS-DR 23 and CELL-DR 23 can be used for multiple cycles of M^{x+} removal from aqueous media. Also, the developed complexing materials were tested for Mn^{2+} , Zn^{2+} , Fe^{3+} , and Cr^{3+} removing from tannery wastewater.

Keywords: cellulosic materials; complexing process; adsorption; metal ions; reutilization; wastewater; environmental sustainability

1. Introduction

Water pollution is a significant issue that generates extensive global discussion [1,2]. In response, green technologies offer promising solutions for enhancing wastewater treatment [3–6]. These innovative approaches not only tackle the challenges associated with removing inorganic contaminants but also contribute to a more sustainable future [7–9]. One particularly effective method is adsorption through complexation interactions, which provides a straightforward and efficient way to eliminate hazardous metals [10–12]. By embracing these technologies, we can substantially improve water quality and safeguard the environment [13]. Traditional wastewater treatment

methods are often quite expensive and tend to generate additional waste byproducts [14]. These methods typically require significant financial resources for infrastructure, operation, and maintenance. Moreover, the processes can result in leftover sludge and other materials that need further disposal or treatment, adding to the overall environmental impact and costs involved [15]. As a result, there is increasing interest in discovering more sustainable and cost-effective solutions [16,17]. Natural materials and those derived from waste are increasingly evaluated for their abundance, bioavailability, and environmental benefits [18]. Cellulose, the most natural polymer existing in nature, shows potential for use in wastewater treatment for pollutant removal [13,19–21]. The main functional groups of cellulose are hydroxyl (existing in the C2, C3 and C6 positions in each linear structure of glucose residue) and carbonyl; together with others, they enhance the adsorption of heavy metals and organic pollutants through mechanisms like surface complexation, ion exchange, and physical adsorption [22–24]. This property makes cellulose materials effective adsorbents for contaminants in wastewater [25–27].

Cellulose together with its modified structures was created to obtain a new category of adsorbents with improved properties for retaining metal ions [5,28–33]. At the same time, more laboratory investigations are necessary for the modification and isolation of cellulose [34–36]. Also, various chemicals are required to extract cellulose, making the process expensive and often environmentally unsustainable [37–39].

So, the main objective of the research presented in this article is to prepare complexing polymers, which can offer flexible working conditions together with good stability, selectivity, high concentration capacity, high metal ion retention capacity and simple operation and without producing additional pollution by leaching of the complexing agent. Despite the great importance of the adsorption capacity of the adsorbent material, the regeneration step for process economy is much less studied than adsorption studies [40].

Thus, until this study, the potential of complexing celluloses MS-DR 23 and CELL-DR 23 has not been employed in Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} removal. As a consequence, the main objective of this study was to obtain new chelating cellulose using DR 23 as chelating agent, cellulose powder (CELL) and cellulosic material derived from shredded maize stalks (MS) for Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} removal.

In the experimental part, pH influence, kinetic and equilibrium studied were employed for obtained new complexing cellulose. Also, the stability of the MS-DR 23 and CELL-DR 23 was verified in the presence of the desorption agents in acidic and basic medium. UV-VIS method was used to estimate the concentration of the complexing agent retained onto cellulosic materials. Thus, the adsorption performances of the resulting materials were tested for adsorption of divalent metal ions (Zn^{2+} and Mn^{2+}) and trivalent (Cr^{3+} and Fe^{3+}) from polluted aqueous matrices via AAS method. Metal interaction at different pH value and masses of complexing celluloses as well as kinetics and equilibrium study were evaluated. Regeneration and reuse of complexing CELL-DR 23 and MS-DR 23 in five metal adsorption/desorption cycles were done. Also, MS-DR 23 and CELL-DR 23 for depollution real wastewater was tested.

2. Materials and Methods

2.1. Chemicals

Cellulose powder (Supelco), direct red 23 -[[6-[(4-acetamidophenyl)diazenyl]-5-hydroxy-7-sulfonatophthalen-2-yl]cabamoylamino]-4-hydroxy-3-phenyldiazenyl naphthalene-2-sulfonate) 30% dye content (Sigma Aldrich), Certified reference materials (CRM) mono-element solutions of 1000 mg/L $\text{Zn}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$, 37 % HCl and 50% NaOH from Merck were used in experimental study.

2.2. Equipment

For UV-VIS spectrometric analysis, a DR/5000 TM spectrometer (Hach Lange, Germany) was utilized. For the quantitative determination of metal ions, a Perkin Elmer PinAcle 900T atomic absorption spectrometer (Perkin Elmer, Norwalk, CT, USA) was employed. The pH of the supernatant and buffer solutions was checked using a HI 255 pH-meter Hanna Instruments, Nijverheidslaan, Belgium. For the preparation of the complexing celluloses, as well as for the adsorption of metals onto the complexing celluloses, a GFL 3017 horizontal mechanical shaker (Bremen, Germany) was used.

2.3. Preparation of Working Solutions

The stock solution 1g/L was obtained by weighing an appropriate amount of DR 23, dissolving it in water and subsequently transferring to a 500 ml volumetric flask. Aqueous solutions of different HCl concentrations were prepared by diluting 37% HCl solution for the activation and purification of cellulose materials. Simultaneously, phosphate, acetate and carbonate buffer solutions were prepared. The buffer solutions employed were: phosphate buffer for pH=2.0, acetate buffer for pH=4.2, acetate buffer for pH=6.0, phosphate buffer for pH=8.0 and carbonate buffer for pH=10.2, respectively.

2.4. Procedure for Purification and Activation of Cellulosic Materials

Initially, the powdered cellulose (≈4g) was washed and hydrated and subsequently transferred to a glass column over which 30 mL of 4M HCl was passed with a flow rate of 0.4 mL/min. After activation and purification, the cellulose was washed with demineralized water until the reaction for chloride ion was negative (verification with 0.02 M $\text{Hg}_2(\text{NO}_3)_2$ solution). The cellulose was removed from the column, filtered and left to dry for 48 h at laboratory temperature. Acid treatment of shredded maize stalk was done according to methodologies developed in previously study [41].

2.5. Procedure for the Complexation of Cellulosic Materials in Function of pH

Over 0.05 g MS and CELL, 0.02 L of 315 mg/L DR 23 solution were added. The pH of the studied solutions was pH=2.0, 4.2, 6.0, 8.0 and 10.2. The pH=7 was obtained when DR 23 is dissolved in ultrapure water. The mixtures obtained were stirred at 175 rpm, 75 min at $T=25\pm 2^\circ\text{C}$. At the end of the stirring, the mixtures were filtered and the amount of DR 23 that was not retained on the cellulose mass was determined spectrometrically. All experimental data were done in duplicate, and the average data were used to determine adsorption capacity (Q_e). The adsorption capacity Q_e (mg/g) obtained at equilibrium for DR 23 adsorption on MS and CELL was determined by applying the equation (eq) 1:

$$Q_e = \frac{(C_i - C_t)V}{m} \quad (1)$$

where: C_i and C_t (mg/L) represent the initial concentration of DR 23 and concentration at time (t), m (g) is the mass of dry MS and CELL, V (L) is the volume of DR 23.

2.6. Procedure for the Adsorption of Complexing Agent in Function of Contact Time on Cellulosic Materials

Thus, 0.05 g of MS and CELL were weighed into Erlenmeyer flasks. Then 0.02 L of 315 mg/L DR 23 solution pH=2 was added to the cellulosic materials. The mixtures obtained were stirred at the following interaction times: 15, 30, 45, 60, 75, and 90 min, and stirred at 175 rpm ($25\pm 2^\circ\text{C}$). After stirring, the celluloses loaded with DR 23 were filtered on filter paper and the amount of DR 23 retained in the resin mass was determined from the filtered solutions using the calibration curve obtained at the linearity of the spectrometric method. All experimental data were done in duplicate, and the average data were used to determine Q_t .

The adsorption capacity evaluated in function of the interaction time (Q_t (mg/g)), was calculated with the eq 2:

$$Q_t = \frac{(C_i - C_t)V}{m} \quad (2)$$

where: C_t (mg/L) represents the concentration of DR 23 at time t in the solution.

The percentage of metals removed from aqueous matrices by MS-DR 23 and CELL-DR 23 were determined applying eq 3:

$$R (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3)$$

where C_i (mg/l) and C_e (mg/l) are the initial and equilibrium concentration of metal ions in supernatant solutions.

2.7. Procedure Used to Obtain Complexing Celluloses in Function of Initial Concentration of DR 23

Over 0.05 g of cellulosic material, fixed volumes of 0.02 L DR 23 of 105, 210, 315 and 420 mg/L were added in 250 mL Erlenmeyer flasks. The obtained mixtures were stirred for 75 min at 175 rpm, and at $T=25\pm 2^\circ\text{C}$. At the end of stirring time, the celluloses in complexed form with DR 23 were filtered and the amount of DR 23 that was not retained in the mass of material was determined spectrometrically based on the calibration curve presented in the experimental part.

2.8. Procedure for Evaluating the Stability of Complexing Celluloses MS-DR 23 and CELL-DR 23

For the stability evaluation, samples of 0.5 g each loaded with 39.9 mg/g CELL-DR 23 and 52.4 mg/g MS -DR 23 were used in this regard. Subsequently, 30 mL 2M HCl and NaOH solution were added to the weighed samples. The resulting mixture were stirred in Erlenmeyer flasks for 30 min at 175 rpm ($T=25^\circ\text{C}$). After 30 min of stirring, the samples were kept in standby for 5 min and subsequently filtered. The filtered solutions were analyzed spectrometrically in the 200-800 nm range.

2.9. Experimental Procedure for the Adsorption of Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} using MS-DR 23 and CELL-DR 23 in Function of pH Solutions

For the removal of Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+} on MS-DR 23 and DR 23-CELL, respectively, ≈ 0.05 g of MS-DR 23 (56 mg DR 23/g) and CELL-DR 23 (41 mg DR 23/g) were stirred with 0.03 L solutions pH=2.0; 6.0; 8.0; 10.2 in which the concentration of Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} was 2.5 mg/L. The mixtures were stirred for 90 min at 175 rpm ($T=25\pm 2^\circ\text{C}$). After stirring, the mixtures were filtered and the metal concentration was determined by AAS method.

2.10. Procedure for Evaluating Contact Time for Metal Ions Adsorption

To study the time required to reach adsorption equilibrium for the removal of Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+} on MS-DR 23 and DR 23-CELL, over 0.5 g of complexing material, 0.05L solution pH=10 with a concentration of 4 mg/L was added. The mixtures thus obtained were stirred at 175 rpm ($T=25\pm 2^\circ\text{C}$) using the batch method at different time intervals of 15, 30, 45, 60, 75 and 90 min. The equilibrium was considered reached at the time when the concentration of Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+} in the measured samples remained constant.

2.11. Procedure for Metal Ions Retained on MS -DR 23 and CELL-DR 23

For this purpose, 0.05g sample of CELL-DR 23 and MS-DR 23 was subjected to mechanical stirring for 90 min at 175 rpm ($T=25\pm 2^\circ\text{C}$) with 0.03L pH=10 containing 0.5; 1.0; 1.5; 2.0; 2.5; 3.0 and 4 mg/L Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} . At the end of stirring time, the concentration of unretained Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+} in the mass of the MS-DR 23 and CELL-DR 23 was determined using AAS method. Data obtained at equilibrium were modulated applying eq 1 and Langmuir eq 4.

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \quad (4)$$

where: Q_{max} and b are Langmuir constants correlated with the adsorption capacity and affinity of complex materials (mg/g) and (L/mg).

2.12. Procedure for Desorption of Metal Ions from Complexing Materials

The complexing materials loaded with 1.11 mg/g Mn^{2+} , 0.81 mg/g Cr^{3+} , 0.87 mg/g Zn^{2+} , 1.16 mg/g Fe^{3+} on CELL-DR 23 and 1.17 mg/g Mn^{2+} , 1.09 mg/g Cr^{3+} , 1.07 mg/g Zn^{2+} and 1.18 mg/g Fe^{3+} on MS-DR 23 \approx 0.05 g were subjected to desorption with 30 mL of 0.25, 0.5 and 1M HCl. The obtained solutions were stirred in Erlenmeyer flasks for 30 min in batch mode at 175 rpm ($T=25\pm 2^\circ C$). After 30 min of stirring, the samples were left to stand for 5 min and subsequently filtered, and the filtered solutions were analysed by AAS.

2.13. Procedure for Reuse of Complexing Materials in Several Adsorption-Desorption Cycles

The complexing materials \approx 0.05 g CELL-DR 23 and MS-DR 23 were stirred with 0.05 L mixed solution of 2 mg/L metal ions at pH=10 for 90 min at 175 rpm ($T=25\pm 2^\circ C$). After 90 min of stirring, the mixtures were centrifugation and supernatant solution was collected and subjected to AAS analysis to determine the concentration of unretained metal ions on the mass of complexing material. Simultaneously, the solid phases loaded with metal ions were subjected to regeneration. After each regeneration step, the solid phases were reused for five adsorption/desorption cycles.

2.14. Procedure for Using Complexing Materials in Wastewater Depollution Processes

For the application of complexing materials in wastewater depollution processes 0.05 g of material loaded with 39.9 mg/g CELL-DR 23 and 52.4 mg/g MS-DR 23 were used. The obtained mixtures were stirred for 90 min at 175 rpm ($T=25\pm 2^\circ C$) with 0.05L wastewater matrix. Herein, wastewater matrix was obtained by mixing 0.025L tannery wastewater with 0.025L buffer solution pH=10. The initial concentration (C_i , mg/L) of Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+} before adsorption on complexing materials was determined and the values obtained were: 1.9 ± 1.75 mg/L Cr^{3+} , 1.2 ± 1.06 Fe^{3+} , 0.7 ± 0.55 mg/L Mn^{2+} and 0.35 ± 0.22 mg/L Zn^{2+} , respectively. At the end of the experiment the mixtures were filtered and the concentration of metal ions that was not retained on the complexing materials was determined by AAS.

3. Results and Discussion

3.1. Linearity Study of Analytical Methods Used for the Quantitative Determination of the Complexing Agent DR 23 and for Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+}

The spectrometric methods described below were used to estimate the concentration of the complexing agent and metal ions in the studies aimed at developing the experimental model.

Thus, the linearity of the UV-VIS spectrometric method was studied to determine the concentration of the complexing agent used for complexation of the cellulose materials. In this regard, the calibration curve was examined in the concentration range that were varied between 14 - 70 mg/L DR 23. From the graphical representation of the absorbance (A) read at the 504 nm wavelength (λ) in function of the concentration (C), the calibration line $A = 0.0339C + 0.0736$ was obtained and the value of the correlation coefficient (R^2) was 0.9992. The high value of R^2 suggests a good linearity of the UV-VIS method over the entire concentration range studied, indicating that Beer's law was verified (Figure 1).

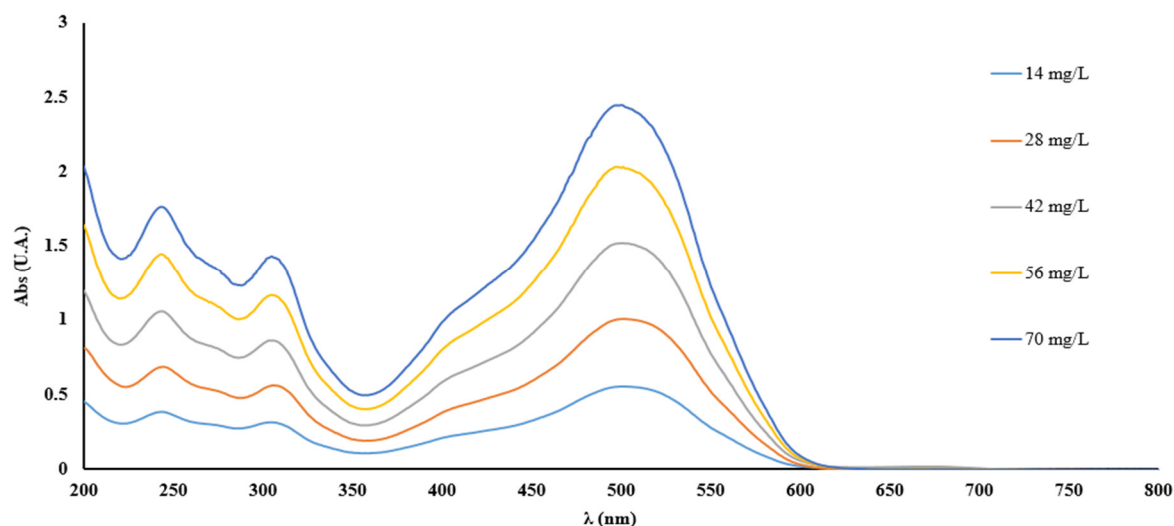


Figure 1. UV-VIS spectra of DR 23 recorded in the range 200–800 nm.

The linearity of the atomic absorption spectrometric method (AAS) was verified in range 1 - 5 mg/L. The solutions for establishing the linearity of the AAS method were prepared from 1000 mg/L CRM stock solution of $\text{Zn}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, and $\text{Cr}(\text{NO}_3)_3$. Initially, working solutions were obtained and these were prepared as follows: 5 mL from each CRM solution of 1000 mg/L was quantitatively transferred to a 50 mL volumetric flask to create the working solution. Subsequently, the solutions for plotting the calibration curves were obtained by diluting the working solution to achieve 1, 2, 3, 4, and 5 mg/L of Mn^{2+} , Zn^{2+} , Cr^{3+} and Fe^{3+} necessary for the linearity study of the AAS method.

The wavelengths used for the detection of the studied metal ions were: 279.48 nm for Mn^{2+} , 213.86 nm for Zn^{2+} , 357.87 nm for Cr^{3+} and for Fe^{3+} the selected wavelength was 248.33 nm. To obtain the calibration curves, each standard solution corresponding to each metal ion was analyzed. The calibration curves were obtained representing the absorbance intensity vs the concentration in mg/L and are graphically represented in the Figure 2.

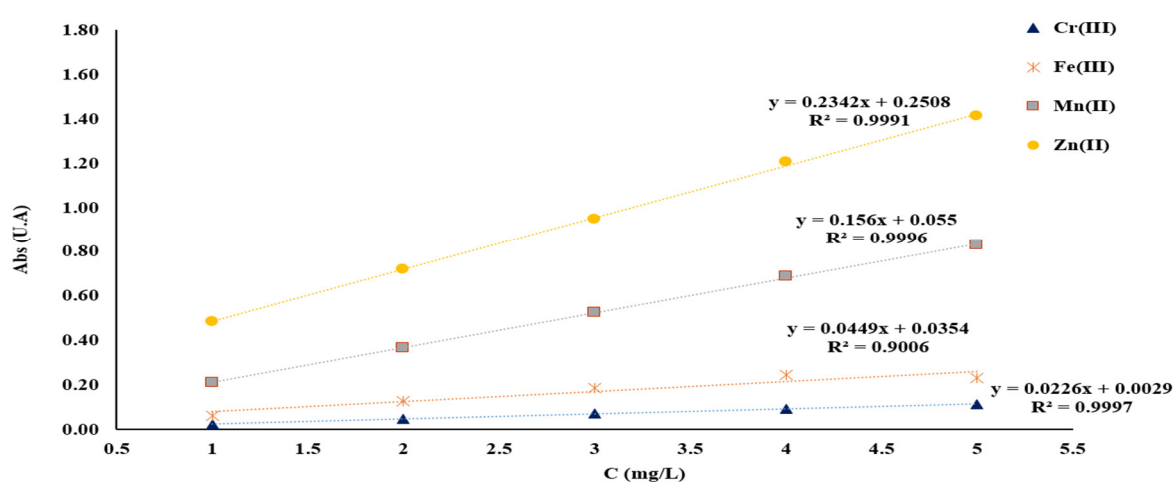


Figure 2. Calibration curves of Cr^{3+} , Fe^{3+} , Mn^{2+} and Zn^{2+} .

3.2. Adsorption Experiments of Complexing Agent DR 23

In order to obtain new complexing materials (MS-DR 23 and CELL-DR 23), experimental parameters such as: the influence of the pH in aqueous medium, the contact time between the two phases and the initial concentration of the complexing agent (DR 23) can significantly impact on the

retention of DR 23 on the two celluloses studied. Thus, in order to evaluate the adsorptive potential of cellulosic materials, laboratory studies were conducted under batch conditions using aqueous systems containing the complexing agent.

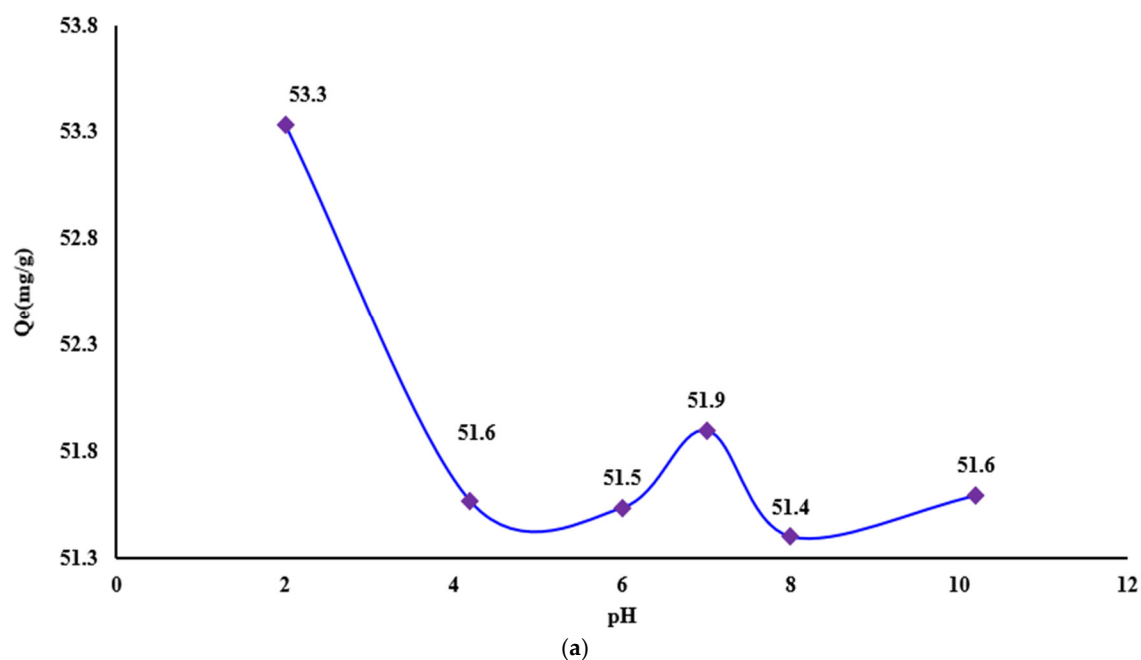
3.2.1. Mechanism Proposed for Obtained Complexing Materials

The proposed mechanism according to the literature data [26,42] for the adsorption of the complexing agent DR23 on the cellulose existing in the structure of the shredded maize stalk (MS) and on the synthetic cellulose (CELL) can be described as follows:

- (i) Hydrogen bonds may form between the strong hydrogen donor of DR 23 and the hydrogen acceptor of the hydroxyl group in the cellulose structure;
- (ii) Electrostatic interactions may occur when the negatively charged sulfate ($-\text{SO}_3^-$) groups interact with the $-\text{OH}_2^+$ group in the cellulose material structure in a strongly acidic environment;
- (iii) At acidic pH values, the hydroxyl groups became protonated and act as positively charged species fixing the negative molecules of complexing agent DR 23 through an ion exchange equilibrium.
- (iv) Meanwhile, as pH increases from acidic to a weakly acidic region deprotonation occurs, and the positive character of the $-\text{OH}_2^+$ group is transformed into a negative one $-\text{O}^-$, causing cellulose to attracts positive ions/positive molecules. Consequently, in this stage the complexing agent DR 23 cannot be fixed by an ion exchange equilibrium. This behavior allows the functional groups act as negatively charged species, binding the positive metal ions present in the solution.

3.3. Study of Complexation Cellulosic Materials in Function of pH

In the experimental studies, initially the retention of the complexing agent (DR 23) on the cellulosic materials was studied based on the pH of the aqueous solution. The results obtained are presented in Figure 3 (a, b).



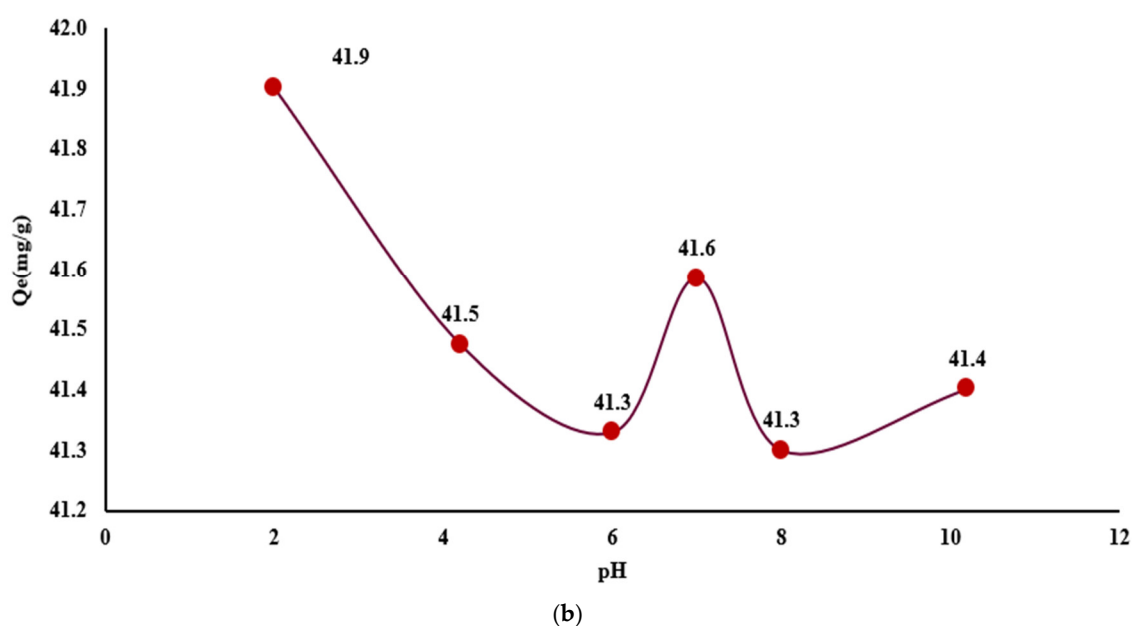


Figure 3. Adsorption of the complexing agent in function of the pH solution on the MS (a) and CELL (b).

The obtained results suggest that the adsorption of the complexing agent on MS and CELL is influenced by the pH of the aqueous matrix. The complexing agent is an anionic compound containing two sulfonic groups that at pH=2 is dissociated. Thus, an increase in the adsorbed amount is observed at pH=2 with 53.3 mg/g for MS and 41.9 mg/g for CELL, which decreases with pH increasing at 4 and 6, reaching a new adsorption maximum at pH=7 (51.9 mg/g for MS and 41.6 mg/g for CELL), and also at pH=10 (51.6 mg/g MS and 41.4 mg/g for CELL).

This behavior can be attributed to the fact that in a strongly acidic environment, the hydroxyl groups present in cellulose structure are protonated and became involved in electrostatic interactions with the sulfonic groups (SO_3^{2-}) of the complexing agent DR 23. As the pH of the buffer solutions increases, the deprotonation of the hydroxyl groups occurs until their dissociation, leading to a decrease in the degree of adsorption is observed due to the electrostatic repulsions that arrive if we take into account the behavior of the ionizable groups at pH 4 and 5.

Thus, we can conclude that the efficiency of the complexation process is governed mainly by electrostatic interactions. Moreover, at pH > 2, the retention of the complexing agent can be achieved through hydrogen bonds as well as through other physical interactions, since new maxima of adsorption were obtained. Based on these observations, it was established that the optimal pH with the most significant adsorption capacities of 53.3 mg/g for MS and 41.9 mg/g for CELL at pH=2 was achieved. This value was used in the subsequent experimental studies for the complexation of the cellulose materials.

3.4. Influence of Contact Time Between the MS/CELL and DR 23

Another parameter studied was the contact time (t), necessary to reach the equilibrium state, between the liquid and solid phases. The experimental results are presented in Figure 4 and were obtained using the following experimental conditions at 315 mg DR 23/L, at pH=2, and contact time varying from 15, 30, 45, 60, 75 to 90 min on 0.05g MS/CELL.

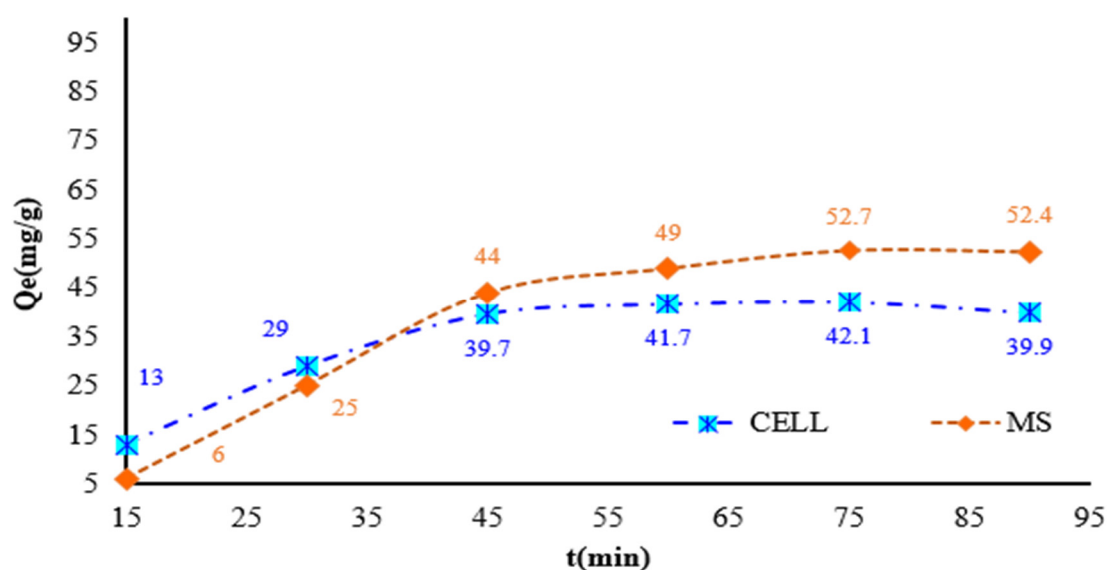


Figure 4. Influence of the contact time required to complex the cellulose existing in the shredded maize stalk and synthetic cellulose.

From Figure 4 it can be observed that the contact time influences the adsorption process of DR 23 on the tested cellulosic materials. Thus, as the contact time increases, the amount of complexing agent (Q_e) increases on the mass of adsorbent material. This increase is more evident in the first stage; according, this initial stage lasts up to 45 min, during with the amount of complexing agent retained is 39.7 mg/g of DR 23 on CELL and 44 mg/g DR 23 on MS. After this stage the adsorption process of the complexing agent becomes significantly slower, and the adsorption capacity of DR 23 increases up to 52.4 mg/g on MS and 39.9 mg/g for CELL. Based on these experiments it can be concluded that a contact time of 75 min is sufficient to reach the equilibrium state for both cellulosic materials studied.

3.5. Influence of the Initial Concentration of the Complexing Agent on the MS and CELL

The adsorption process of DR 23 on the MS and CELL (Figure 5) was achieved gradually increasing the initial concentration of DR 23. It was found that the adsorption on the studied celluloses is influenced by the initial concentration varying from 105 to 420 mg/L. The adsorption capacity values in the case of DR 23 adsorption on MS were 21 mg DR 23/g MS, 38 mg DR 23/g MS, 56 mg DR 23/g MS and 56.8 mg DR 23/g MS. For CELL, the following experimental values were: 19.2 mg DR 23/g CELL, 38.5 mg DR 23/g CELL, 41 mg DR 23/g CELL and 42 mg DR 23/g CELL.

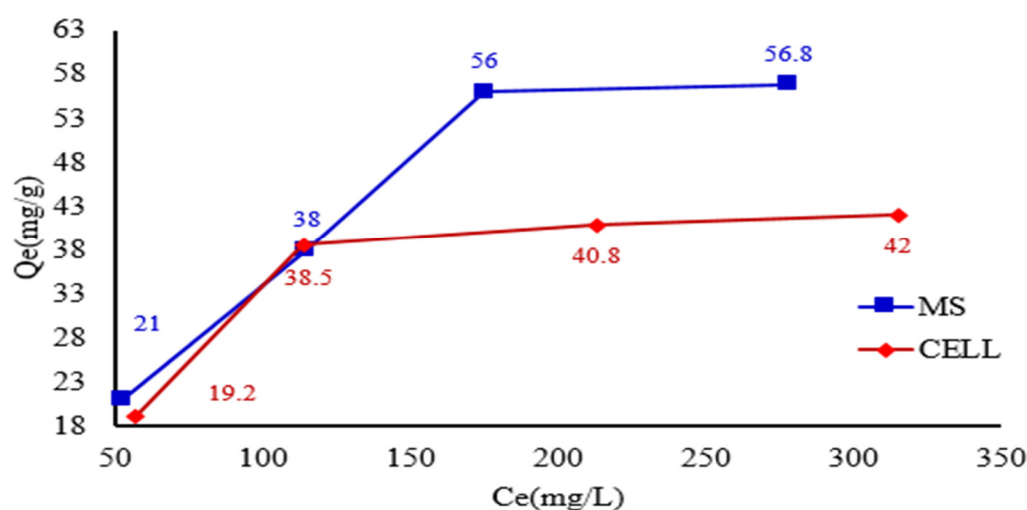


Figure 5. Influence of initial concentration of DR 23 for adsorption of MS and CELL.

Studies on the Stability of Complexing Materials

It is known that when the complexing material exceeds its adsorption capacity, it is considered that it is exhausted and must be regenerated for a new adsorption/desorption step. Furthermore, once the complexing materials are exhausted, the metal ions in the tested solutions are not retained, and this aspect is monitored by measuring their concentrations in the supernatant.

Initially, the stability of the complexing materials was checked in the presence of the desorption agents 2M HCl and NaOH. The complexing materials were weighed and transferred into an Erlenmeyer flask to which the previously mentioned desorption agents were added and stirred for 30 min. At the end of the stirring time, the materials were filtered and the filtered solutions were analyzed spectrometrically. The amount of complexing agent in the eluent solution was checked based on the following calibration curve $A = 0.0339C + 0.0736$.

Stability in acidic and basic environments was chosen because wastewaters are mostly acidic, while at $\text{pH} > 7$ are basic or alkaline. It was found that the complexing agent DR 23 remains fixed in the mass of the two celluloses when the two desorption agents were added, therefore, they can be regenerated when they are involved in the retention of metal ions using one of the two desorption agents tested.

3.6. Tested of Complexing Materials for Metal Ions Adsorption as a Function of pH Medium

The functional groups present in the structure of the complexing agent (Figure 6) can demonstrate an affinity for metal ions by binding the metal ions through a complexation or chelation mechanism.

Thus, the adsorption mechanism between the metal and the complexing materials can be explained by considering the following hypotheses: DR 23 contains two azo groups ($-\text{N}=\text{N}-$) that can bind metals when the azo groups donating an electron pair, chelating or complexing the metal; (ii) by diffusion in the porous structure of the complexing materials; (iii) by ion exchange between the SO_3^{2-} groups of DR 23 that are not involved in the first adsorption stage of DR 23. Simultaneously, the two materials subjected to complexation contain $-\text{OH}$ groups. Also, the MS has in its structure other macro components containing groups such as carboxyl $-\text{COO}^-$, amino ($-\text{NH}_2$), sulfhydryl ($-\text{SH}$), etc., which can retain metal ions from the solution through a complexation mechanism [43].

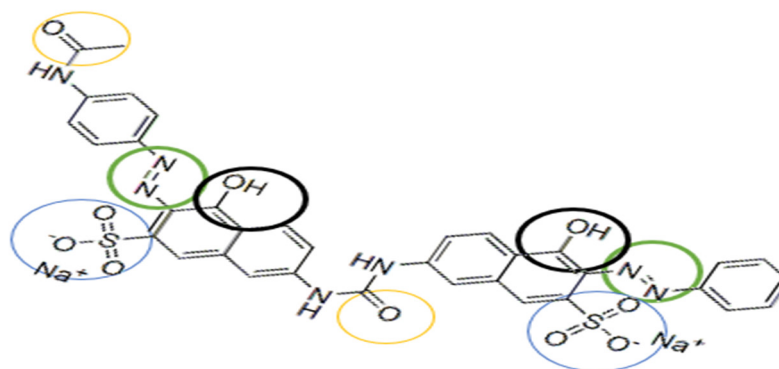


Figure 6. Chemical structure of the complexing agent used for metal ions complexation.

Is known from literature studies that complexing materials change their degree of dissociation in function on the pH of the solution used [42]. Thus, pH influences not only the solubility of metal ions and organic compounds but also the degree of dissociation of the functional groups presents in the structure of the cellulosic material studied in adsorption experiments.

Therefore, to avoid the precipitation of metal ions at higher pH levels > 8 where most metal ions precipitate in the form of hydroxides and the adsorption process is not involved in the adsorption of metal ions, buffer solutions at pH=2.0; 4.2; 6.0; 8.0 and pH=10.2 were used.

The new complexing materials (MS-DR 23 and CELL-DR 23) were tested for the removal of metal ions from aqueous matrices as well as to evaluate their applicability in wastewater decontamination experiments at different pH value (Figure 7). Thus, the influence of pH on the adsorption process of metal ions on MS/CELL and in the DR 23 form was studied at pH= 2.0; 4.2; 6.0; 8.0 and 10.2 using 2.5 mg/L M^{x+} , 0.05g of CELL- DR 23 and MS-DR 23 along with 0.03 mL buffer solution.

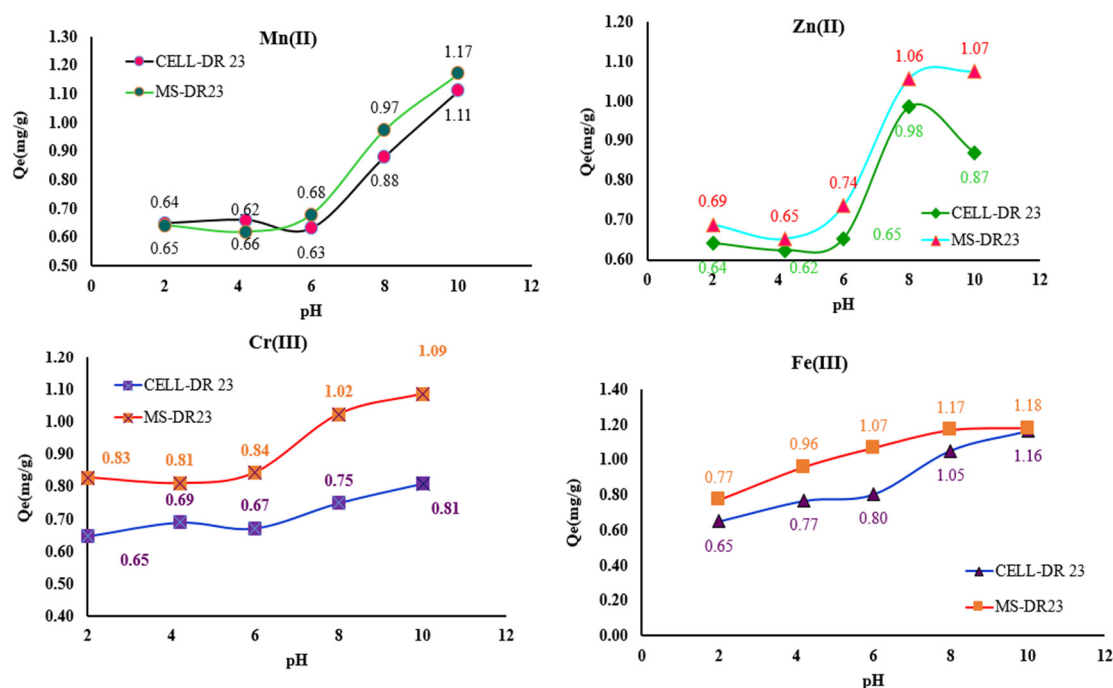


Figure 7. Adsorption behavior of metal ions on complexing materials at different pH values of aqueous matrix.

From the data presented in Figure 7, it can be seen that the retention of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} on the surface of MS-DR 23 and CELL-DR 23 occurs with the highest efficiency at pH 8 and 10. It is also observed that the best adsorption capacity of MS-DR 23 and CELL-DR 23 at pH=10 was done. Taking into consideration the Q_e (mg/g) values at pH=10 the following affinity series

$\text{Fe}^{3+} > \text{Mn}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+}$ was obtained for MS-DR 23. Meanwhile, for CELL-DR 23 the affinity obtained was: $\text{Fe}^{3+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$.

3.7. Study of the Influence of Contact Time Between Metal Ions and Complexing Materials

The contact time between the two phases (liquid/solid) is a decisive parameter of the adsorption process that must be studied. The experimental results obtained in the study of the influence of the contact time between MS-DR 23 and CELL-DR 23 and aqueous solutions containing Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} were evaluated and the results are presented in Figure 1 and Table 1 from the Supplementary Materials.

Table 1. Parameter of Langmuir model obtained for adsorption of Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} using complex cellulose materials.

Model	Mn ²⁺	Fe ³⁺	Cr ³⁺	Zn ²⁺	Mn ²⁺	Fe ³⁺	Cr ³⁺	Zn ²⁺
Langmuir	CELL-DR 23				MS-DR 23			
R ²	0.9825	0.9999	0.9978	0.9953	0.9978	0.9999	0.9968	0.9922
Q _{max} (mg/g)	1.31	1.27	1.15	1.21	1.36	1.27	1.28	1.29
R _L (g/L)	0.07	0.005	0.14	0.12	0.03	0.005	0.04	0.13

In this study, it was found that with the increase of initial pH from 2 to 10 of the mixtures subjected to adsorption, the adsorption capacity of the two functionalized materials studied increased. This variation is determined by the fact that with the increase in the pH of the initial solution, the dissociation of the carbonyl (-C=O) and hydroxyl (-OH) groups existing in the structure of the DR 23 complexing agent occurs, which become negatively charged and can bind the positive metal ions (M^{x+}) in the solution subjected to adsorption. In order to keep the degree of dissociation of the functional groups relatively constant, a carbonate buffer solution (pH=10) was used. Taking into account best Q_e value all adsorption studies presented subsequently were carried out at pH=10. The contact time necessary to reach the equilibrium state was studied by batch method in the range of 15 to 90 min. The concentrations of the supernatant solutions obtained at 15, 30, 45, 60, 75 and 90 min, respectively were determined using the calibration line obtained for each metal studied separately in the concentration range of 1-5 mg/L. In this regard, the calibration lines: $A = 0.2342C + 0.2508$ for Zn^{2+} , $A = 0.156C + 0.055$ for Mn^{2+} , $A = 0.0449C + 0.0354$ for Cr^{3+} and $A = 0.2342C + 0.2508$ for Fe^{3+} were used to determine the concentration of the studied metal ions retained on the mass of complexing materials.

Thus, according to the experimental results, the amount of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} fixed in the mass of CELL-DR 23 and MS-DR 23 increases with the increasing of contact time and remains constant when equilibrium is reached. It is observed that this increase is more pronounced in the first stage and varies depending on the metal ions studied. In the first stage, the adsorption capacity increased from 0.5 to 1.08 mg/g for Mn^{2+} , from 0.6 to 1.2 for Fe^{3+} , from 0.24 to 0.9 for Cr^{3+} , and from 0.18 to 0.93 for Zn^{2+} during adsorption on CELL-DR 23.

The experimental results for MS-DR 23 in the first stage, varying the contact time and keeping the rest of the operational parameters constant, Q_i varied as follows: from 0.24 to 1.07 mg/g Mn^{2+} , from 0.54 to 1.14 mg/g for Fe^{3+} , from 0.36 to 1.2 mg/g for Cr^{3+} and from 0.2 to 1.1 mg/g for Zn^{2+} ions.

After this first stage, the adsorption of metal ions becomes slower, observing a flattening trend due to reaching chemical equilibrium, and the retained percentages for Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} vary insignificantly for both tested materials, results which are presented in Table S1 from the Supplementary Materials.

Based on these observations, any time greater than 60 min can be used in subsequent adsorption studies, but considering that the structure of functionalized polymers is not sufficiently homogeneous and assuming that access of metal ions to the functionalized groups would be more

difficult. Therefore, a contact time of 90 min would be sufficient to reach the equilibrium state in order to evaluate the adsorption capacity of the tested materials at maximum capacity.

3.8. Study of the Influence of the Initial Metal Ion Concentration on the Binding Capacity of Complexing Materials

Simultaneously, experimental studies at equilibrium were conducted using batch method. For this purpose, 0.5 g of CELL-DR 23 and MS-DR 23 and 0.05 L of 0.5; 1; 1.5; 2; 2.5; 3 and 4 mg/L pH=10 at 175 rpm for 90 min.

The adsorption capacity (Q_e , mg/g) of metal ions retained on 0.05 g of CELL-DR 23 were: 0.25; 0.54; 0.82; 1.02; 1.14; 1.20; 1.21 mg/g for Mn^{2+} .

For Fe^{3+} adsorption capacity were: 0.29; 0.58; 0.88; 1.15; 1.23; 1.20 and 1.20 mg/g, respectively. In the case of Cr^{3+} ions, the adsorption capacity found were: 0.2; 0.5; 0.7; 0.8; 0.9; 1.0 and 1.02.

Also, during the investigation of Zn^{2+} ions adsorption on CELL-DR 23, the following values were obtained : 0.25; 0.51; 0.70; 0.87; 0.93; 1.02 and 1.08 mg/g.

At the same time, in the case of MS-DR 23 the following adsorption capacities were calculated for the studied metal ions, obtaining the following values: 0.28; 0.57; 0.85; 1.14; 1.26; 1.26 and 1.32 mg/g for Mn^{2+} . For Fe^{3+} Q_e determined were 0.30; 0.59; 0.89; 1.18; 1.24; 1.25 and 1.26 mg/g respectively.

In case of Cr^{3+} the adsorption capacity calculated were: 0.30; 0.60; 0.80; 1.10; 1.17; 1.2 and 1.22 mg/g. For Zn^{2+} the adsorption capacity varied as between 0.26; 0.53; 0.66; 0.86; 0.99; 1.06 to 1.13 mg/g.

Analyzing the results presented in Figure 9, it is found that the isotherms obtained experimentally regarding the adsorption of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} on CELL-DR 23 and MS-DR 23 are nonlinear for the studied concentration range, observing two main adsorption regions.

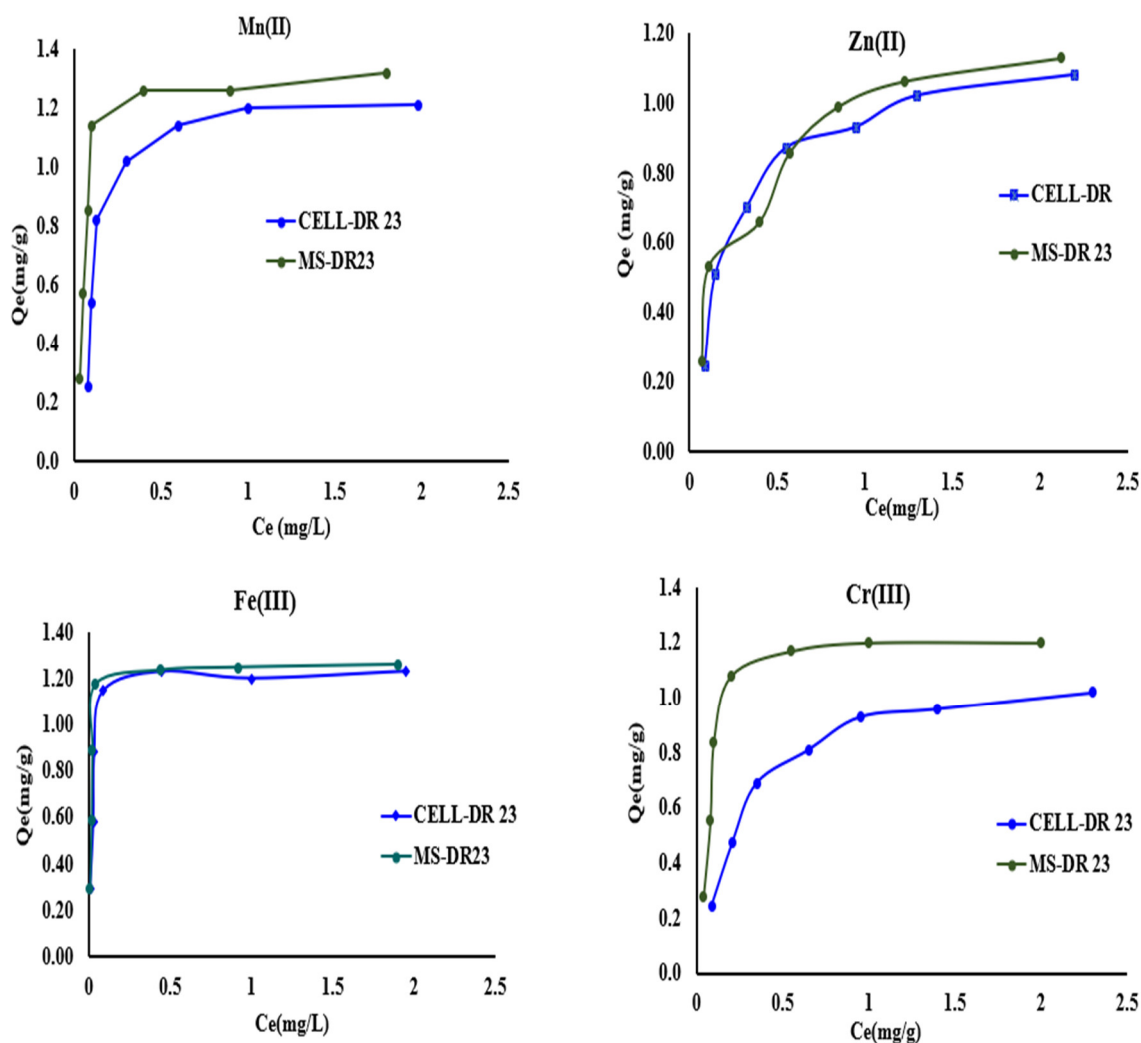


Figure 9. Experimental isotherms for the adsorption of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} ions for CELL-DR 23 and MS-DR 23 respectively at pH=10 of the tested solution.

The first region corresponding to 0.5-2 mg/L followed by the saturation level at 3 and 4 mg/L for Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} .

At the same time, it was found that MS-DR 23 has a better adsorption capacity than the CELL-DR 23, and this increase is all the more evident at higher C_i of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} in the tested solution.

3.9. Study of the Langmuir Adsorption Isotherm

The relationship between the amount of metal ion retained per unit mass of adsorbent material and the corresponding concentration of the solute at equilibrium represents the adsorption isotherm.

Thus, the experimental data obtained at equilibrium were modeled based on the Langmuir mathematical model that describes the adsorption process on homogeneous surfaces until a saturated is obtained on the surface of the tested material.

The parameters of the Langmuir isotherm were determined graphically from the slope and intercept of the graphical representation $C_e/Q_e = f(C_e)$. The results obtained are presented in Figure S1 from Supplementary materials.

From the data presented in Table 1, it is observed that the values of the R^2 are greater than 0.9800. This indicates that the CELL-DR 23 and MS-DR 23 respectively are considered adsorbents with a homogeneous surface on which Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} can be retained through a specific

complexation and adsorption interactions until obtaining a monolayer that covers the surface of CELL-DR 23 and MS-DR 23.

Based on the Langmuir model, the maximum adsorption capacities Q_{max} (mg/g) were determined, obtaining the following values: 1.31 mg/g Mn^{2+} , 1.27 mg/g Fe^{3+} , 1.15 mg/g Cr^{3+} and 1.21 mg/g Zn^{2+} for the CELL-DR 23. For MS-DR 23, the Q_{max} values determined by fitting the experimental data were: 1.36 mg/g Mn^{2+} , 1.27 mg/g Fe^{3+} , 1.28 mg/g Cr^{3+} and 1.29 mg/g Zn^{2+} . It is noted that the Q_{max} (mg/g) values of MS-DR 23 are higher than for CELL-DR 23, results presented in Table 1.

One possible explanation can be that the MS-DR 23 was better loaded with complexing agent and also chemical groups from its structure that was not employed in DR 23 adsorption can employing to complexing metal ions. Moreover, the value of the R_L constant (g/L) between 0 and 1 indicates a favorable adsorption process of the studied metal ions on MS-DR 23 and CELL-DR 23.

3.10. Regeneration of Exhausted Complexing Materials with Metal Ions

In this part, the exhausted materials were regenerated with 0.25, 0.5 and 1M HCl to release Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} loaded on MS-DR 23 and CELL-DR 23. Herein, the MS-DR 23 and CELL-DR 23 were subjected to adsorption / recovered / regenerated / reused in a new adsorption/desorption process. The complexing materials were subjected to further loading by the batch method with 2 mg/L of Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} , respectively. After 90 min of stirring at 175 rpm ($T=25\pm 2^\circ C$) in batch mode, the mixtures were centrifuged, filtered and solid phase was kept for desorption studies. For the MS-DR 23, the tested samples used were 0.05g of 1.17 mg/g Mn^{2+} , 1.2 mg/g Fe^{3+} , 1.09 mg/g Cr^{3+} and 1.07 mg/g Zn^{2+} , respectively. For the reuse of CELL-DR 23, the solid samples employed were loaded with 1.11 mg/g Mn^{2+} , 1.16 mg/g Fe^{3+} , 0.81 mg/g Cr^{3+} and 0.87 mg/g Zn^{2+} were tested. Following the desorption studies, it is observed that when 0.5 M HCl is used, Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} existing on the MS-DR 23 and CELL-DR 23 are desorbed in a proportion over 90%. The data obtained at desorption of Mn^{2+} , Zn^{2+} , Fe^{3+} and Cr^{3+} are presented in Figure 10.

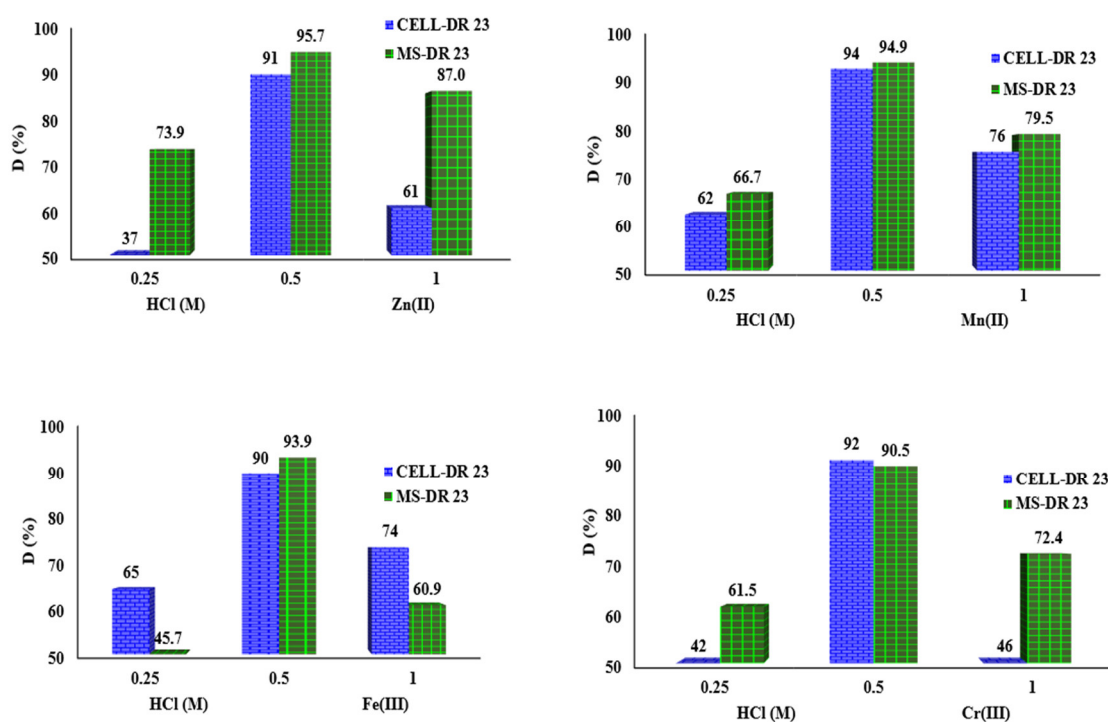


Figure 10. Desorption of Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} from MS-DR 23 and CELL-DR 23 using 0.25, 0.5 and 1M HCl.

For the CELL-DR 23 loaded with Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} , the effective desorption percentages were detected as follows: 91% Zn^{2+} , 94% Mn^{2+} , 90% Fe^{3+} and 92% Cr^{3+} when 0.5 M is used.

Simultaneously, a decrease in the desorption efficiency was observed when 0.25 and 1M HCl was used for both tested complexing materials.

Considering the results obtained, the following regeneration studies for materials regeneration loaded with metals (MS-DR 23- M^{x+} and CELL-DR 23- M^{x+}) were performed using 0.5M HCl.

3.11. Reutilization of Complexing Materials in Multiple Adsorption/Desorption Cycles

Acid effluents polluted with metal ions can be treated by applying the principles of circular economy and involve the reducing of metal concentration and recovering the materials for subsequent use. For this propose CELL-DR 23 and MS-DR 23 were stirred with 2 mg/L mixed solution of Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} and from the supernatant solutions the concentration of metal ions was determined by AAS method while the solid phases were subjected to regeneration with 0.5 M HCl solution in order to recover and reuse them in a new adsorption/desorption cycle. The results obtained are presented in Figures 11 a, b.

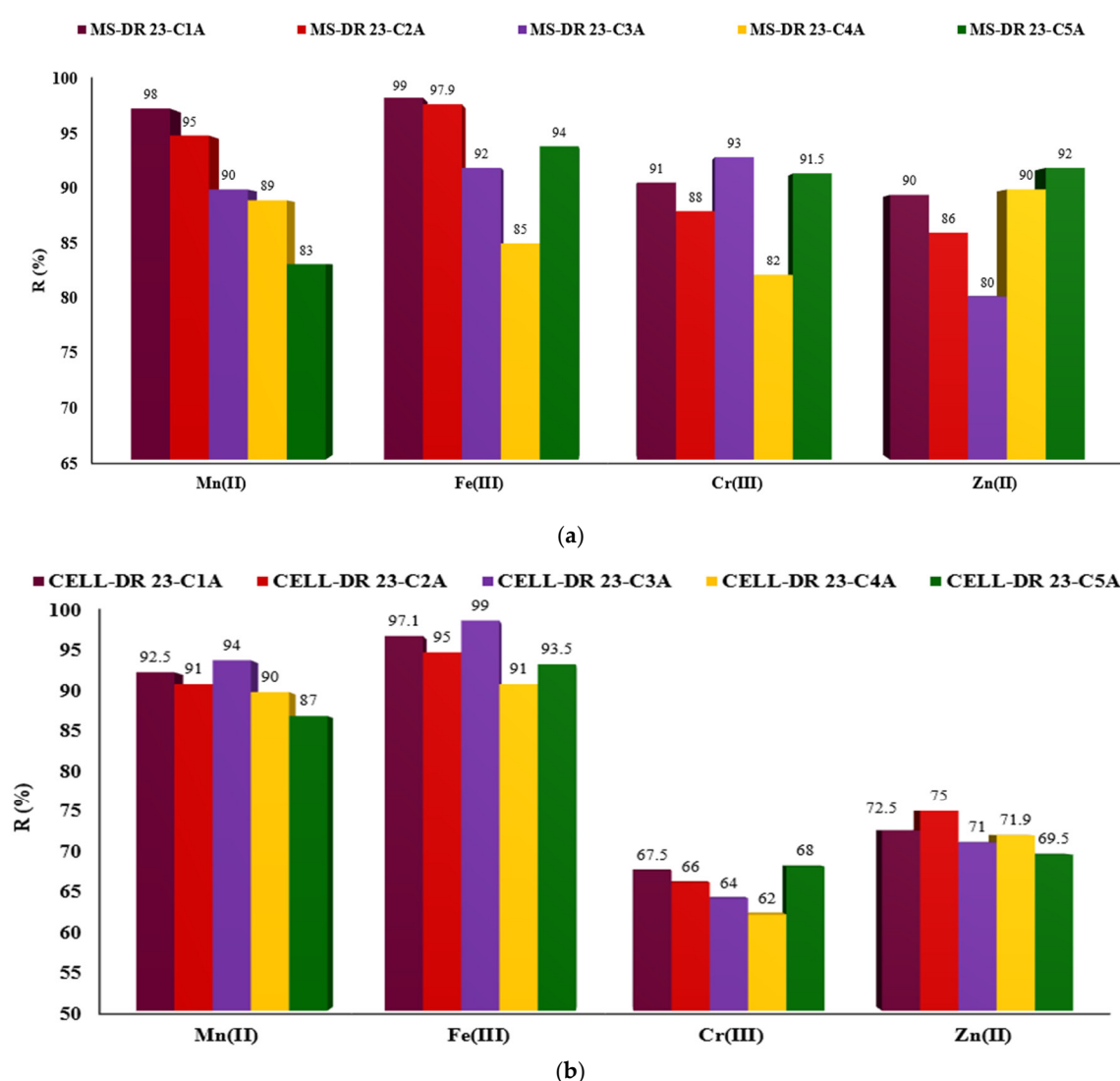


Figure 11. Reutilization of MS (a) and CELL (b) in DR 23 form in five adsorption cycles.

So, the chelated materials (CELL-DR 23 and MS-DR 23) loaded with Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} , were regenerated and reused in five adsorption/desorption cycles. It was found that for a new reuse from one to five adsorption cycles, a variation was obtained more evident for MS-DR 23 if we compare with CELL-DR 23 as is presented in Figure 11 a,b.

3.12. Applications of Complexing Materials on Tannery Wastewater Matrix

During the study, the best adsorption capacity of the complexing materials, it was found at pH=10 and the applications of complexing materials on tannery wastewater matrix were performed at this value.

Considering this, when adsorption studies were conducted on tannery wastewater, a mixture in a 1:1 ratio with the acetate buffer solution (pH=10) was done obtaining a pH=9.9 of the mixed solution. At the same time, C_i of metal ions before adsorption on MS-DR 23 and CELL-DR 23 was determined, obtaining 1.9 ± 1.75 mg/L Cr^{3+} , 1.2 ± 1.06 Fe^{3+} , 0.7 ± 0.55 mg/L Mn^{2+} and 0.35 ± 0.22 mg/L Zn^{2+} , respectively.

It is also known that the adsorption capacity of complexing materials decreases for metals with a large ionic radius due to the steric effect. Thus, metals with a small ionic radius enter in the porous structure of the complexing materials and interact with the functional groups present in their structure. The For studied metal ions ionic radius decreased as: $0.55 \text{ \AA} \text{ Fe}^{3+} < 0.62 \text{ \AA} \text{ Cr}^{3+} < 0.67 \text{ \AA} \text{ Mn}^{2+} < 0.74 \text{ \AA} \text{ Zn}^{2+}$. Therefore, the affinity sequence of the studied metals could be governed by their ionic radius.

For metals that possess the same charge, the tendency is to retain them according to their ionic charge. This means that for divalent metal ions, the metal with the smallest ionic radius should easily diffuse into the structure of the complexing cellulose polymers and be involved in the complexation reaction with the functional groups present in the structure of chemically modified materials. Analyzing the results presented in the Figure 12, the CELL-DR 23 and MS-DR 23 are promising materials for the simultaneous removal of the Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} , one in the presence other.

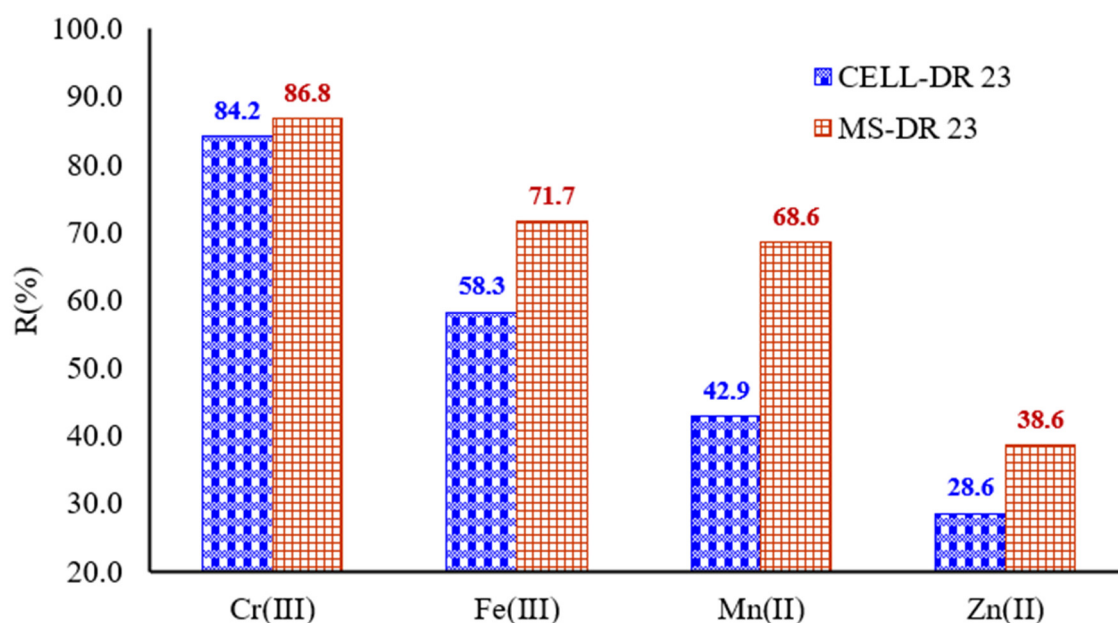


Figure 12. Adsorption of metals from tannery wastewater on CELL-DR 23 and MS-DR 23, respectively.

Additionally, the removal percentage exceeded 28% for the studied metals, these results are influenced by the C_i of Mn^{2+} , Fe^{3+} , Cr^{3+} and Zn^{2+} present in the wastewater matrix.

So, it was observed that MS-DR 23 and CELL-DR 23 significantly reduced the concentration of metals as follows with: 68.6 % Mn^{2+} , 71.7% Fe^{3+} , 86.8 % Cr^{3+} and 38.6 % Zn^{2+} for MS-DR 23. Simultaneously, CELL-DR 23 indicated a rate of adsorption by 42.9 % Mn^{2+} , 58.3 % Fe^{3+} , 84.2 % Cr^{3+} and 28.6 % Zn^{2+} . Taking into consideration those results we can see that the concentration gradient of metals influence adsorption process on developed materials.

4. Conclusions

In conclusion, as observed, one of the most significant influences on the adsorption process regarding the retention of the complexing agent DR 23 on the two celluloses is determined by the pH of the aqueous solution which impacts the hydroxyl groups as well as on the ionization process of the DR 23 complexing agent. As observed at pH = 2, the retention of the complexing agent occurs with the highest efficiency.

Thus, pH affects the adsorption process of the complexing agent by influencing the degree of dissociation of the functional groups of the surface binding centers in the structure of the adsorbent celluloses, leading to the modification in the equilibrium characteristics of the adsorption process.

Thus, at sufficiently low pH values, the surface of cellulosic materials is protonated and the DR 23 molecules are negatively charged, which attracts them to the cellulose binding centers. Due to electrostatic attraction forces, the DR 23 molecule is adsorbed on the cellulose mass.

Also, analyzing the results obtained by varying each experimental parameter evaluated in the adsorption of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} ions on CELL-DR 23 and MS-DR23, respectively, it can be said that: the adsorption capacity increases with pH increasing of the studied solution; the increase in the initial concentration of Zn^{2+} , Mn^{2+} , Cr^{3+} and Fe^{3+} ions in the concentration range 0.5-4 mg/L leading to an increase in the adsorption capacity of CELL-DR 23 and MS-DR23, respectively; the increase of contact time between the phases of the adsorption system led to an increase in the amount of metal ion on both CELL-DR 23 and MS-DR 23. This increase is more pronounced in the first adsorption stage which is observed up to 60 min, after this stage the adsorption process becomes slow and the adsorption capacity varies insignificantly, indicating that equilibrium has been reached.

Cellulosic complexing materials show a good stability in acidic and basic environments up to the tested concentration of 2M. Regeneration studies were conducted with increased efficiency when using 0.5 M HCl. At the same time, the complexing materials have proven their susceptibility to multiple reuses. In conclusion, for equal concentrations of metal ions, the complexing polymers exhibit a preferential affinity for Cr^{3+} and Fe^{3+} in the presence of the two divalent metals (Mn^{2+} and Zn^{2+}). Moreover, the concentration gradient influenced the adsorption capacity of the metal ions evaluated on the tested materials.

So, this study is dedicated to loading and complexing cellulose materials and application of complexing celluloses to metal removal from aqueous matrices.

Supplementary Materials: The following supporting information can be downloaded at: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Influence of contact time for metal ions removal onto MS-DR 23 and CELL-DR 23; Table S1: Percentage removal of metal ions onto MS-DR 23 and CELL-DR 23.

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