chemistry proceedings

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Proceeding Paper

Chitosan-Based Biosorption: A Sustainable Approach for Heavy Metal Removal from Wastewater †

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† Presented at the 29th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-29); Available online: https://sciforum.net/event/ecsoc-29.

Abstract

This study investigates the application of natural chitosan as an efficient adsorbent for the removal of heavy metals from aqueous solutions. Experimental results showed that Mn(II), Co(II), and Ni(II) ions were effectively retained on the chitosan surface. Kinetic analysis revealed a preferential adsorption order of Co(II) > Mn(II) > Ni(II), following a pseudo-second-order model with rapid kinetics. Equilibrium adsorption capacities were influenced by initial concentration, temperature, and pH. Thermodynamic analysis indicated that the adsorption process was exothermic and physical in nature. Overall, chitosan proved to be a promising and cost-effective adsorbent for water decontamination.

Keywords: chitosan; heavy metals; wastewater; adsorption

Academic Editor(s): Name

Published: date

Citation: Lansari, I.; Tizaoui, K.; Benguella, B. Chitosan-Based Biosorption: A Sustainable Approach for Heavy Metal Removal from Wastewater. *Chem. Proc.* **2025**, *volume number*, x. https://doi.org/10.3390/xxxxx

1. Introduction

The rapid development and continuous growth of industrial activities have significantly increased the release of toxic pollutants into the environment [1]. Among them, heavy metal contamination of water resources has become one of the most pressing environmental concerns, attracting global attention due to its persistence, non-biodegradability, and harmful effects on ecosystems and human health [2]. As a result, the search for reliable and efficient techniques to treat wastewater contaminated with heavy metals has become a major research priority.

Over the past decades, various conventional treatment methods have been applied for the removal of heavy metals from aqueous solutions, including chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and evaporation [3,4]. While these methods have demonstrated effectiveness under certain conditions, they are often associated with limitations such as high operational costs, energy consumption, incomplete metal removal, and the generation of secondary waste. These drawbacks have motivated researchers to explore alternative technologies that are not only efficient but also economically and environmentally sustainable.

Among the available approaches, adsorption has emerged as one of the most effective and promising techniques for wastewater removal [5–8]. Its advantages include high removal efficiency, operational simplicity, and the possibility of using low-cost and abundant natural adsorbents. In recent years, increasing attention has been directed toward the utilization of bioadsorbents derived from renewable biomass sources [9–11]. In particular, chitosan, a biopolymer obtained through the deacetylation of chitin has gained significant interest due to its low cost, biodegradability, non-toxicity, and high adsorption capacity [12]. The presence of amino and hydroxyl functional groups in its structure enhances its affinity for heavy metal ions, making it a versatile and eco-friendly material for water treatment applications.

In this context, the present study was designed to evaluate the adsorption potential of natural chitosan as a low-cost and sustainable adsorbent for the removal of selected heavy metals from aqueous solutions. By employing supports derived from the recycling of fishery by-products, this work aims to contribute to the development of environmentally responsible strategies for wastewater remediation.

2. Materials and Methods

FTIR Spectroscopy

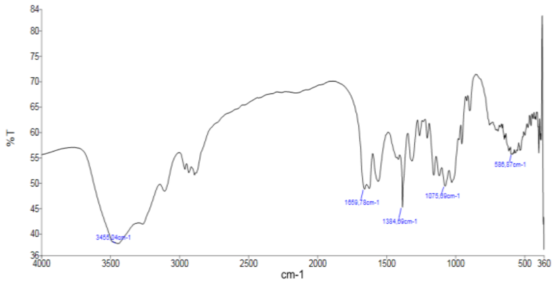

Figure 1. FTIR spectroscopy of chitosan.

Table 1. FTIR spectrum attribution [13].

Band (cm^{-1})	Attribution
3469	N-H and OH streching
2925–2975	C-H of CH_2 and/or CH_3 groups
1644	C=O groups
1550	N-H groups
1343	C-H bending in CH_3 groups
1305	C-N Bond stretching vibration
1154	C-O bendig vibration
1079	C-O-C Bond stretching vibration
597	C-H group bending vibration

3. Results and Discussion

3.1. Effect of Contact Time

Figure 2 illustrates the evolution of the amounts of metals adsorbed as a function of the contact time between chitosan and the aqueous solutions containing Mn(II), Ni(II), and Co(II) ions. The adsorption kinetics exhibited similar trends, characterized by a rapid uptake of metal ions during the initial minutes of contact, followed by a slower increase until equilibrium was reached. This rapid initial phase can be attributed to the large number of available active sites on the chitosan surface at the beginning of the process, which gradually become saturated over time [14].

At equilibrium, chitosan showed a higher affinity toward Co(II), followed by Mn(II), and then Ni(II). The equilibrium contact time was the same for all three metals, approximately 180 min. The maximum adsorption capacities reached 30 mg/g for Co(II), 22.91

mg/g for Mn(II), and 19.38 mg/g for Ni(II), confirming the preferential adsorption order Co(II) > Mn(II) > Ni(II).

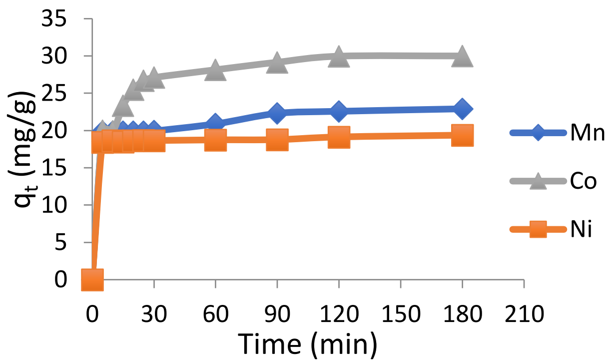

Figure 2. Effect of contact time of the adsorption of heavy metals on chitosan C_{metal} = 100 mg/L, $V_{solution}$ = 300 mL, $m_{chitosan}$ = 1 g, pH = neatural, T ambient, stirring speed = medium. Same results was obtained in previous investigation [15].

3.2. Kinetic Study

The adsorption rate constants of the different heavy metals onto chitosan were determined graphically using three kinetic models. The first-order model was expressed as:

- 1st order: log $(q_e - q_t)/q_e$ = f(t) pour la détermination de K_v (Equation (1))
- Pseudo 2nd order: t/q_t = f(t) pour la détermination de K′ (Equation (2))
- 2nd order: $1/(q_e - q_t)$ = f(t) pour la détermination de K. (Equation (3))

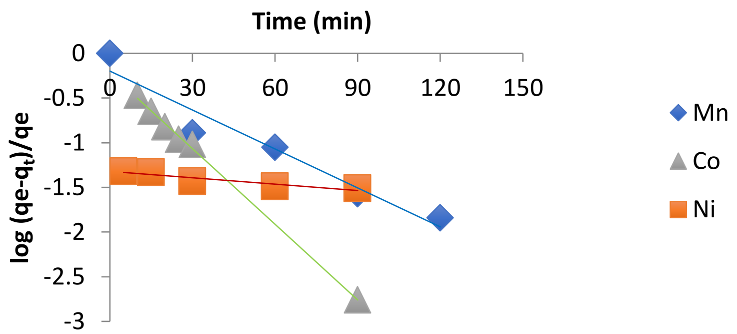

Figure 3. First order kinetic model.

Table 2. Results of first order rate constent K_v.

Metal	R^2	K_v (min^{-1})
Mn	0.97	$33.42.10^{-3}$
Co	0.98	$64.86.\ 10^{-3}$
Ni	0.94	$5.47.10^{-3}$

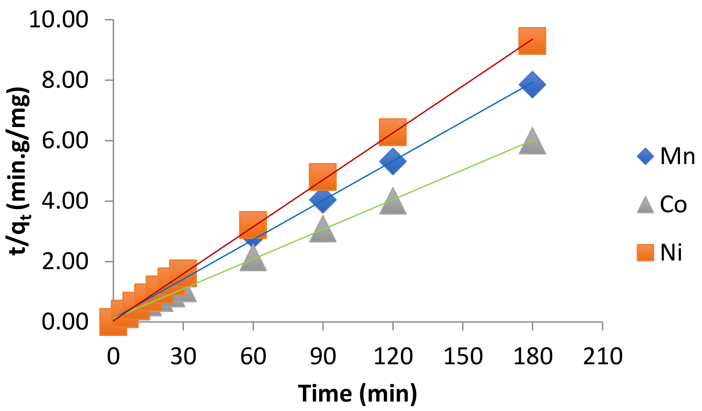

Figure 4. Pseudo second order kinetic model.

Table 3. Results of the pseudo second order rate model.

Metal	q_e (mg/g)	K′ (min^{-1}.g/mg)	R^2
Mn	23.04	81.23.10^{-4}	0.99
Co	30.53	4.65. 10^{-3}	0.99
Ni	19.31	32.79. 10^{-2}	0.99

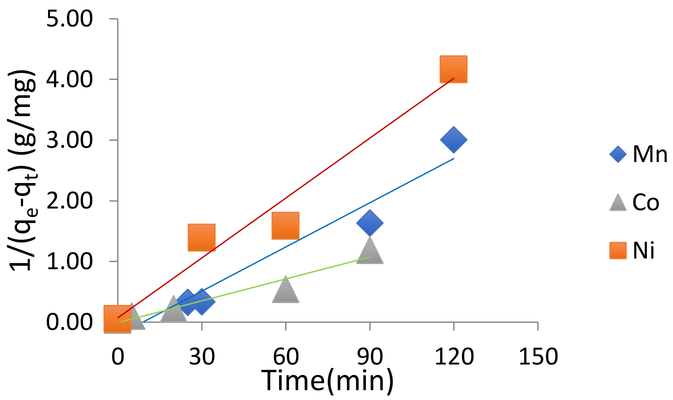

Figure 5. Pseudo second order kinetic model.

Table 4. Results of the second order rate model.

Metal	q_e (mg/g)	K (min^{-1}.g/mg)	R^2
Mn	−4.59	24.26.10^{-3}	0.97
Co	−102.04	12.03. 10^{-3}	0.98
Ni	14.29	32.95.10^{-3}	0.98

Based on the results presented in Tables 1, 2, 4, and 5, it can be concluded that the pseudo-second-order model provides the most reliable description of the adsorption kinetics of the different heavy metals onto chitosan. Furthermore, the calculated q_e values are in close agreement with the experimentally determined ones, and the correlation coefficient was found to be as high as 0.99.

3.3. Influence of the Initial Metal Ion Concentration on the Adsorption

To investigate the influence of initial concentration on the adsorption of heavy metals by chitosan, the following concentrations were selected: 30, 50, 70, 100, 300, and 500 mg/L. The curves presented in Figure 6 exhibit similar trends, characterized by a rapid and nearly linear increase in the amount of metal adsorbed at equilibrium as the initial concentration increases [16]. It was observed that the maximum adsorption capacity rises with higher initial concentrations, which can be attributed to the progressive saturation of available adsorption sites on the chitosan surface. The adsorption curves are nearly superimposed, indicating that the equilibrium amounts of metal retained are comparable for each of the tested metals.

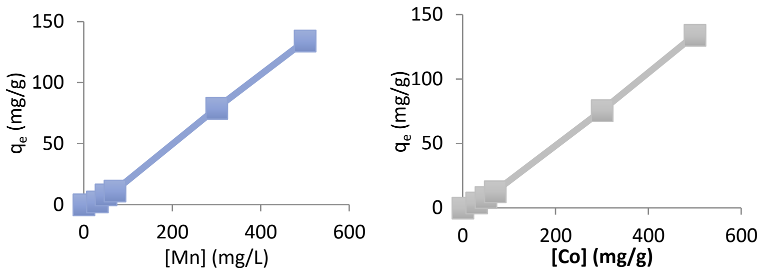

Figure 6. $V_{solution}$ = 300 mL, $m_{chitosan}$ = 1 g, pH = neatural, T ambient, stirring speed = medium.

3.4. Influence of the Temperature of Metal Solutions on the Adsorption

To investigate the influence of temperature on the adsorption capacity of heavy metals onto chitosan, we selected the following temperatures: 10, 20, 30, 40, and 50 °C.

The results of this study, presented in Figure 7, show a slight increase in the metal binding capacity with increasing temperature.

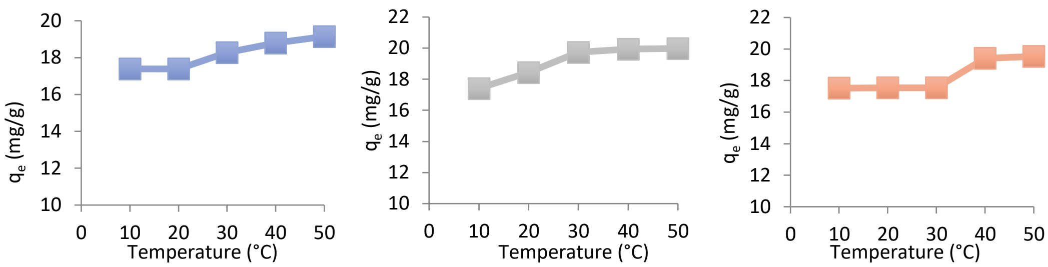

Figure 7. $C_{solution}$ = 100 mg/L, $V_{solution}$ = 300 mL, $m_{chitosan}$ = 1 g, pH = neatural, sttirring speed = medium.

Determination of Thermodynamic Parameters

The adsorption heats of the different heavy metals onto chitosan are determined in Figure 8, which represent the plots of ln Kc versus 1/T, where the temperature is expressed in Kelvin. ΔH was obtained from the slope, while ΔS was calculated from the intercept.

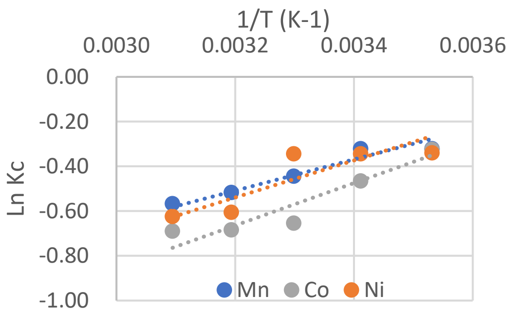

Figure 8. Determination of thermodynamic parameters.

Table 5. Results of the thermodynamic parameters.

Metal	ΔH (KJ/mol)	ΔS (KJ/mol.K)	R^2
Mn	−5.82	−0.023	0.97
Ni	−6.9	−0.026	0.87

Co	−7.90	−0.031	0.93

Table 6. Results of free enthalpy at different temperature.

Metal	T(°C)	10	20	30	40	50
Mn	**ΔG (KJ/mol.K)**	0.69	0.92	1.15	1.38	1.61
Ni	**ΔG (KJ/mol.K)**	0.46	0.72	0.98	1.24	1.50
Co	**ΔG (KJ/mol.K)**	0.88	1.19	1.50	1.81	2.12

According to the results presented in Table 5, the values of ΔH are negative, indicating that the adsorption of heavy metals onto chitosan is an exothermic process. This implies that the system releases heat to the external environment. The relatively low values of ΔH suggest that the process corresponds to physical adsorption.

Furthermore, the ΔS values are also negative, which means that the adsorption of heavy metals on chitosan is accompanied by an increase in order within the system [17]. In other words, the metal ions adsorbed on the surface of the adsorbent are more organized compared to their distribution in the aqueous phase.

3.5. Influence of the Initial pH of Metal Solutions on the Adsorption

To investigate the effect of pH on the adsorption of heavy metals onto chitin and chitosan, the following pH values were selected:

- For manganese: 2, 4, 6, and 8;
- For nickel: 2, 4, 6, and 7;
- For cobalt: 2, 4, 6, and 7.

Figure 9 illustrates the amount of each metal adsorbed at equilibrium as a function of pH.

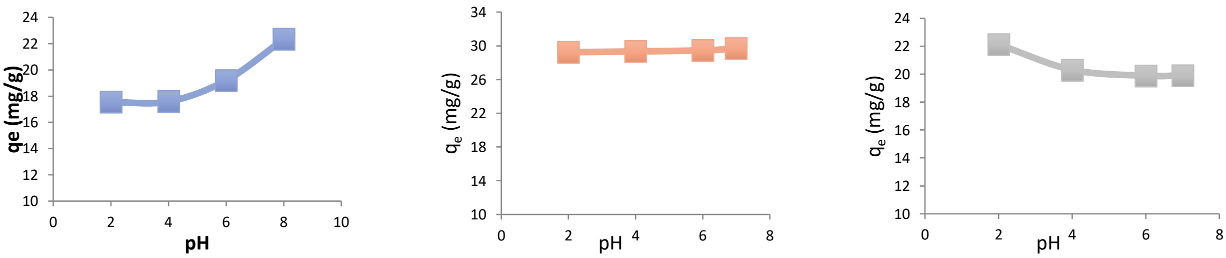

Figure 9. $C_{solution}$ = 100 mg/L, $V_{solution}$ = 300 mL, $m_{chitosan}$ = 1 g, Temperature =ambient, stirring speed = medium.

At acidic pH values, metal ions compete with H_3O^+ ions present in the solution. Due to their higher mobility, hydronium ions are more readily adsorbed than metal ions [18].

At slightly acidic pH (between 4 and 7), the competitive effect of H_3O^+ ions decreases as the pH increases, which explains the higher adsorption of heavy metals by both supports within this pH range.

4. Conclusions

This study demonstrated that chitosan is an efficient and eco-friendly adsorbent for the removal of heavy metals from aqueous solutions. The equilibrium contact time was the same for all three metals, approximately 180 min. The maximum adsorption capacities reached 30 mg/g for Co(II), 22.91 mg/g for Mn(II), and 19.38 mg/g for Ni(II), confirming the preferential adsorption order Co(II) > Mn(II) > Ni(II).

Adsorption kinetics were best described by the pseudo-second-order model, and thermodynamic analysis confirmed that the process is spontaneous, exothermic, and mainly physical in nature. The adsorption capacity increased with metal concentration and was strongly influenced by pH, with optimal removal observed under slightly acidic conditions. Overall, chitosan shows great potential as a low-cost and sustainable material for wastewater treatment applications.

Author Contributions:

Funding:

Institutional Review Board Statement:

Informed Consent Statement:

Data Availability Statement:

Conflicts of Interest:

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