Scholar Publishing Group
Academic Journal of Environmental Biology
https://doi.org/10.38007/AJEB.2022.030406
ISSN 2789-8407 Vol. 3, Issue 4: 45-54

Modified Chitosan Based on Optimized Design in the Treatment of Microbial Leaching Wastewater

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Keywords: Optimized Design, Modified Chitosan, Microbial Treatment, Leaching Wastewater

Abstract: Currently, microbial leaching wastewater has caused immeasurable damage to the environment, so this wastewater must be properly treated to reduce environmental and biological damage. The purpose of this work is to study the physicochemical properties of chitosan, based on the optimized design of modified chitosan in microbial leaching wastewater treatment, using citric acid (CA) as the cross-linking agent chitosan (CTS) and two modified chitosan Chitosan, Chitosan-Citric Acid (CTS-CA) and Chitosan-Citrate-β-Cyclodextrin (CTS-CA-CD) from β-Cyclodextrin (CD) to Explore Modification Mechanisms. At the same time, the prepared modified chitosan was applied to the adsorption research of dye wastewater and heavy metal wastewater. With the increase of reaction temperature, the adsorption capacity of modified chitosan to Ni2+ also increased. It shows that the temperature is beneficial to the adsorption process. The higher the temperature, the better the adsorption effect of modified chitosan on Ni2+. The effect of initial solution pH on the adsorption process showed that at pH 7, the adsorption capacity of CTS-CA for Ni2+ was 33 mg/g, and the adsorption capacity of CTS-CA-CD for Ni2+ was 37 mg/g.

1. Introduction

In recent years, with the development of economy and the acceleration of industrialization, the increasingly serious environmental pollution problem has become a major challenge for human beings, such as water pollution, soil pollution and air pollution [1]. Among them, heavy metal ions are the most important pollutants in water pollution. Due to their serious harm to human health and natural ecosystems, they have attracted widespread attention from the country and all walks of life. The treatment of pollutants in microbial leaching wastewater in the environment Methodological and technical exploration is increasingly becoming the focus of research [2].

At present, the application of modified chitosan in the treatment of microbial leaching wastewater has been studied from many aspects at home and abroad. Sauperl O conducts antibacterial testing to determine inhibition of selected pathogenic microorganisms using the ASTM E 2149-01 standard. The antioxidant activity of the functionalized viscose was studied by DPPH• spectrophotometry. The eugenol-modified chitosan coating was found to impart antibacterial activity to the viscose against Gram-positive and Gram-negative bacteria and fungi, and to inhibit free radicals by introducing antioxidant properties. The chemical and enzymatic modification of chitosan offers many opportunities to incorporate many natural active ingredients into chitosan systems, which provide a good basis for further studies on the functionalization of chitosan for hygiene and medical use [3]]. Shahraki Z M examined whether the accumulation of nitrogen in and around leaching ponds used for on-site wastewater treatment (carryover nitrogen) could be a source of groundwater nitrogen contamination as the pond inflow volume and/or composition changes. In this study, a concrete leaching tank with neutral pH (A, pH 6.9) and one after acid washing (B, pH 3.7) were selected to examine the amount and composition of residual nitrogen in the surrounding soil, and evaluate it. The potential release of this nitrogen in two environmentally relevant leaching scenarios: (i) concrete leaching ponds used as the final discharge unit for aerobic treatment unit (ATU) wastewater; (ii) increased extreme weather events (torrent/heavy rain) flow and dilute the composition of the water flowing into the pool. Core sample analysis indicated that organic nitrogen accounted for a large proportion of total nitrogen (TN) in site A (4.1 +/- 0.6 mg N/g soil) and site B (3.0 +/- 0.4 mg N) part (97.3–99.7%)/g soil); ammonium is the predominant form of inorganic nitrogen present in the field [4]. The existing research points out the direction for the application of the modified chitosan based on the optimized design in the treatment of microbial leaching wastewater.

In this paper, modified chitosan was applied in the treatment of microbial leaching wastewater. On the one hand, the problem of adsorbent desorption is omitted, which effectively avoids the possibility of using a large amount of desorbent in the desorption process and the possibility of re-polluting the water environment by recycling the desorbed heavy metal ions. The heavy metal ions in industrial wastewater are used as the metal source, the supported metal nanocomposites are prepared, and the practical application performance of the composite materials is explored, so as to realize the resource reuse of heavy metal ions in industrial wastewater, turn waste into treasure, and conform to green environmental protection and sustainable development.

2. Research on the Application of Modified Chitosan Based on Optimized Design in the Treatment of Microbial Leaching Wastewater

2.1. Physical and Chemical Properties of Chitosan

(1) Degree of deacetylation (DD)

The degree of deacetylation represents the content of acetyl groups in biopolymers and is one of the most important parameters of chitosan [5]. The physical properties (tensile strength), crystallinity, solubility and thermal stability of chitosan are all related to the distribution of acetyl groups on the main chain. With the increase of DD, on the one hand, the number of free amino groups on chitosan increases, and the intramolecular and intermolecular hydrogen bonds increase; on the other hand, the charge density along the main chain increases, the flexibility of chitosan increases, and the degree of curling increases. Therefore, the degree of deacetylation has a great influence on the physicochemical properties and application degree of chitosan. Generally determined by ultraviolet spectrophotometry, X-ray diffraction, infrared spectroscopy and titration [6-7].

(2) Molecular weight (MW)

The molecular weight of chitosan is related to the number of monomers per polymer molecule, generally between 50 and 2000 kDa, and can be divided into high molecular weight, medium molecular weight, and low molecular weight. Usually, the overall structure of chitosan can be preserved by depolymerization technology. On the basis of modified molecular weight, high molecular weight chitosan was modified to lower molecular weight [7]. Many physical and chemical properties of chitosan, including solubility, viscosity, crystallinity, tensile strength, adsorption and elasticity, are closely related to molecular weight. This also results in the morphologies of the materials prepared with chitosan are quite different, such as films, gels, etc. Generally determined by light scattering method, high performance liquid chromatography and viscosity method [8-9].

(3) Solubility

Chitosan solubility is affected by both DD and MW. On the one hand, chitosan has a high degree of deacetylation and strong hydrophilicity, and more amino groups in the molecular chain are protonated, which increases its solubility; on the other hand, the large molecular weight will cause intra- and intermolecular hydrogen. As the bond increases, the degree of polymerization of the molecular chain increases, resulting in a decrease in solubility. Due to the existence of amino groups, pH is one of the factors affecting the surface electronegativity and solubility of chitosan. When $pH<6.5$, the amino groups on chitosan are easily protonated to form NH_3^+, resulting in a large number of cation adsorption sites, which destroy the hydrogen bonds between molecules, reduce the polymerization between molecular chains, increase the polarity and continuously dissolve. Under acidic conditions, gel-like chitosan is the basis for modification and preparation of composite materials, thereby expanding its potential application range [10-11].

2.2. Hazards of Leaching Wastewater

Antimony ore wastewater refers to mining, beneficiation and smelting wastewater with relatively high concentration. If it is not treated, it will be directly discharged into rivers and infiltrated into groundwater. It will cause different degrees of harm to all living organisms through the food chain. Antimony compounds soluble in water include: $Sb_2(SO_4)_3$, $Sb(NO_3)_3$, $C_4H_4KO\text{-}Sb.1/2H_2O$, $SbCl_3$, $SbCl_5$, etc. Antimony entering the water body is harmful to fish at a concentration of 12 mg/L and toxic to algae at a concentration of 3.5 mg/L[12-13].

Antimony can accumulate in the body, and the antimony element in the body can be excreted from the body through urine and feces. Antimony can be combined with sulfhydryl groups in vivo, reducing the activity of certain enzymes in the body, resulting in the destruction of the balance of ions in the body's cells, causing potassium deficiency in the body's cells. The toxicity of trivalent antimony compounds is stronger than pentavalent antimony compounds. The following is the order of toxicity of antimony and its compounds from small to large: $Sb_2O_3<SbO_3<Sb_2S_5<Sb_2O_3<Sb$[14-15].

2.3. Adsorption Mechanism of Chitosan

At present, there are relatively few studies on the adsorption mechanism of heavy metal elements in chitosan. Due to the different modification methods and modifiers used, different adsorption mechanisms may be caused. In many cases, the adsorption may be a combination of one or more mechanisms, which increases the complexity of the study. At present, there are roughly four mechanisms of action that can be accepted and recognized by most people [16-17].

Adsorption includes physical adsorption, chemical adsorption and bioaffinity of chitosan and its derivatives. Due to the porosity and large specific surface area of chitosan itself, it can have a strong physical adsorption capacity for heavy metal ions. At the same time, a large number of active functional groups on the surface of chitosan also have the effect of chemical adsorption on heavy metal elements.

Chelation is a process in which a metal ion bonds with multiple ligand atoms to form a ring-shaped chelate.

Ion exchange, because the adsorption of heavy metal ions by chitosan and its modified materials is greatly affected by pH value, under neutral and weak alkaline conditions, there are lone pairs of electrons on the amino group, so the adsorption is mainly chelation. Under acidic conditions, the amino group is protonated, and the protonated amino group mainly adsorbs heavy metals through ion exchange [18].

Electrostatic action, under acidic conditions, the amino groups on the surface of chitosan molecules are protonated and have a positive charge, while the metal ion compounds have a negative charge, and the two have electrostatic attraction.

3. Experiment and Research on the Application of Modified Chitosan Based on Optimized Design in the Treatment of Microbial Leaching Wastewater

3.1. Preparation of Modified Chitosan

The preparation process of modified chitosan is carried out in four steps:

The first step: Schiff base reaction between benzaldehyde as amino protecting agent and C2-NH2 to prepare Schiff base chitosan. Accurately weigh 0.5 g of chitosan (degree of deacetylation greater than 75%) and add it to 200 mL of 1% acetic acid solution, stir magnetically until it becomes a transparent gel, and then transfer it to a 300 mL three-necked flask. A certain amount of benzaldehyde was taken in 20 mL of absolute ethanol, and then slowly added dropwise to a three-necked flask, reacted in a water bath at 70 ℃ for 8 h, and the pH was adjusted with 0.50 mol/L NaOH solution to produce a large number of white flocs, respectively. Washed twice with absolute ethanol and deionized water, and dried under vacuum at 65 ℃.

The second step: epichlorohydrin reacts with C6-OH to introduce epoxy groups into the molecular chain to prepare epoxidized chitosan. The obtained Schiff base chitosan was transferred to a 300 mL three-necked flask, 200 mL of 0.50 mol/L NaOH solution was added, and then a certain amount of epichlorohydrin was slowly added dropwise. Washed twice with ionized water and dried under vacuum at 70 ℃.

The third step: the epoxy group in the epoxidized chitosan molecular chain is opened and reacted with the amino groups at both ends of triethylenetetramine to prepare triethylenetetramine grafted chitosan. Transfer the obtained epoxidized chitosan to a 300mL three-necked flask, add 200mL of a certain concentration of NaOH solution, then slowly drop triethylenetetramine into the three-necked flask, control the reaction temperature and reaction time, after the reaction is completed, They were washed twice with absolute ethanol and deionized water, respectively, and dried under vacuum at 70 ℃.

The fourth step: remove the amino protecting group in hydrochloric acid solution, so that C2-NH2 is released again. The obtained triethylenetetramine-grafted chitosan was added to 60 mL of 3% HCl solution, and after magnetic stirring for a certain period of time, washed twice with absolute ethanol and deionized water, and dried in vacuum at 70 ℃. The modified product obtained after acidification was transferred to 100 mL of 0.50 mol/L NaOH solution for alkalization for 3 hours, washed with deionization to neutrality, and dried under vacuum at 70 ℃ to obtain the final modified chitosan.

3.2. Material Characterization

For the acrylic acid modified chitosan magnetic adsorption material, the addition amount of acrylic acid, ammonium persulfate, magnetic nano-iron tetroxide and glutaraldehyde has a great relationship with the adsorption capacity of the composite material. By grafting acrylic acid on chitosan, the amino group is increased. With the increase of the amount of acrylic acid, the adsorption performance of the material is enhanced. However, since acrylic acid is an unsaturated carboxylic acid, too much addition will lead to a low pH value, which will promote a large number of nucleophiles. The combination of amino hydrogen ions is not conducive to the reaction. Ammonium persulfate is the initiator of grafting reaction. With the increase of dosage, the adsorption capacity of the material will first increase and then decrease. This is because the increase of the initiator will lead to the increase of free radicals, which will increase the chance of acrylic acid grafting to the chitosan molecule, but if the amount of the initiator continues to increase, the homopolymerization reaction of the free radicals will increase, and at the same time, it will also increase. It reduces the probability of terminating the reaction and makes the grafting effect worse. The addition of nano-iron tetroxide has an adverse effect on the adsorption effect of the material. It may be due to the decrease of the proportion of acrylic modified chitosan in the unit mass of synthetic materials with the addition of nano-ferric tetroxide. The addition of glutaraldehyde will increase the adsorption capacity first and then decrease, which may be because the increase in the amount of glutaraldehyde will lead to an increase in the amount of chitosan encapsulated on the unit NMR, but if the amount of glutaraldehyde continues to increase, the cross-linking will be excessive. The higher the pore size of the network structure, the smaller the effective adsorption area.

3.3. Adsorption Kinetic Model

Adsorption kinetics is mainly by studying the rate and amount of adsorption at different times, predicting the reaction process and adsorption results, so as to explore the mechanism of the adsorption reaction, which has very important guiding significance in practical applications such as controlling the reaction time and saving the reaction cost. The adsorption reaction is mainly the combined effect of external diffusion, internal diffusion, physical adsorption and chemical adsorption, and the faster frequency oscillation can basically eliminate the effect of external diffusion. A pseudo-second-order (PSO) model was used to study the effect of chemisorption. Internal Diffusion (RID) was used to study the effect of internal diffusion. Its fitting formula is as follows:

$$PFO: \ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$PSO: \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

$$RID: q_t = k_{\text{int}} \sqrt{t} + c \tag{3}$$

q_e and q_t (mg/g) are the adsorption capacity of the material for ions at equilibrium and at time t, respectively; k_1, k_2 and k_{int} are the rate constants of the three models, and k_1, k_2 and q_e can be calculated by t/q_t versus t. The linear equation can be calculated, and k_{int} can be calculated by the regression line of q_t to $t^{1/2}$. After fitting the three models, the correlation coefficient R^2 of the linear equation was calculated, and the adsorption reaction types of the experimental materials for the three ions were judged by comparing the sizes of the three models R^2.

4. Analysis and Research on the Application of Modified Chitosan Based on Optimized Design in the Treatment of Microbial Leaching Wastewater

4.1. The effect of Initial Solution pH on the Adsorption Process

The effect of two modified chitosans on the adsorption of Ni^{2+} under different pH conditions, the results are shown in Table 1.

Table 1. Effect of solution pH on adsorption of CTS and CA-CTS-CD

pH	2	3	4	5	6	7
CTS-CA	4	10	16	27	32	33
CTS-CA-CD	7	13	25	30	36	37

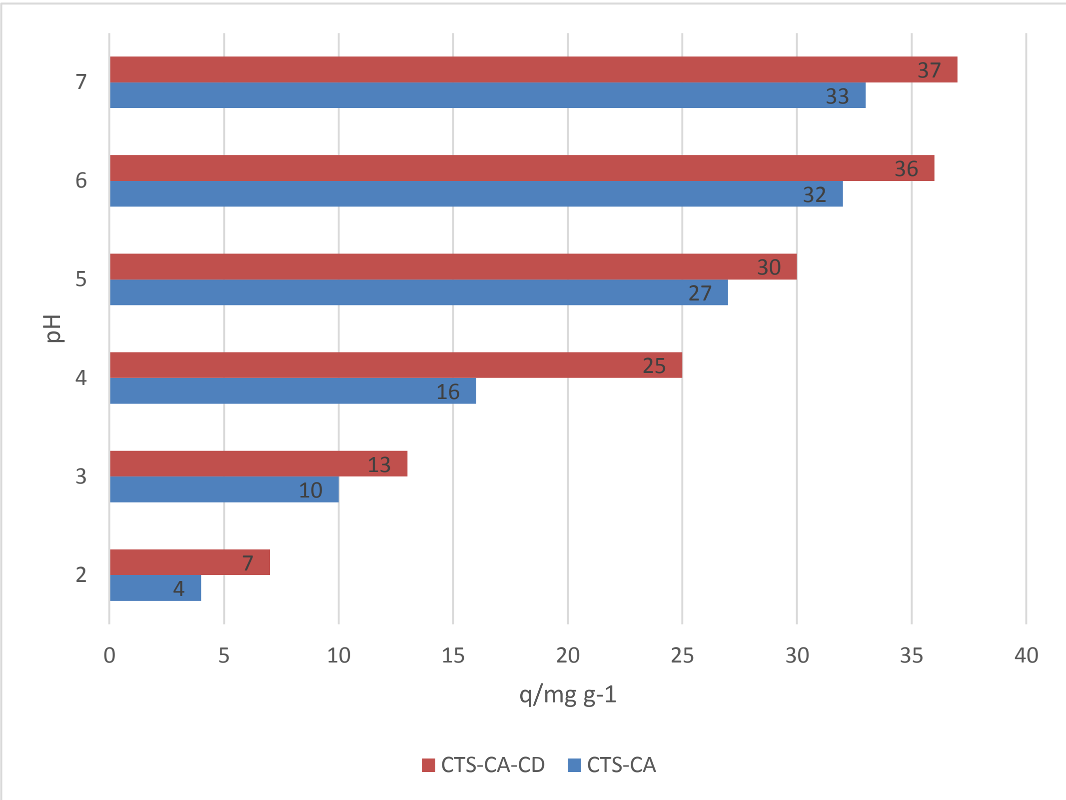

Figure 1. Comparison of solution pH on adsorption of CTS and CA-CTS-CD

It can be seen from Figure 1 that the pH of the solution has a great influence on the adsorption process of Ni^{2+} by the two modified chitosans. The adsorption capacity of both modified chitosans for Ni^{2+} increased with the increase of pH. When the pH is 2, both modified chitosans are dissolved to a certain extent, and the adsorption capacity is small; when the pH is between 3-6, the adsorption capacity of the two modified chitosans for Ni^{2+} increases more. At pH 7, the adsorption capacity of CTS-CA for Ni^{2+} was 33 mg/g, and the adsorption capacity of CTS-CA-CD for Ni^{2+} was 37 mg/g.

4.2. Effect of Temperature on Adsorption Performance

It can be seen from the results in Figure 2 that with the increase of reaction temperature, the adsorption capacity of modified chitosan to Ni^{2+} also increases. It shows that the temperature is beneficial to the adsorption process, and the higher the temperature is, the better the adsorption effect of modified chitosan on Ni^{2+} is. This is consistent with the trend of molecular motion with temperature.

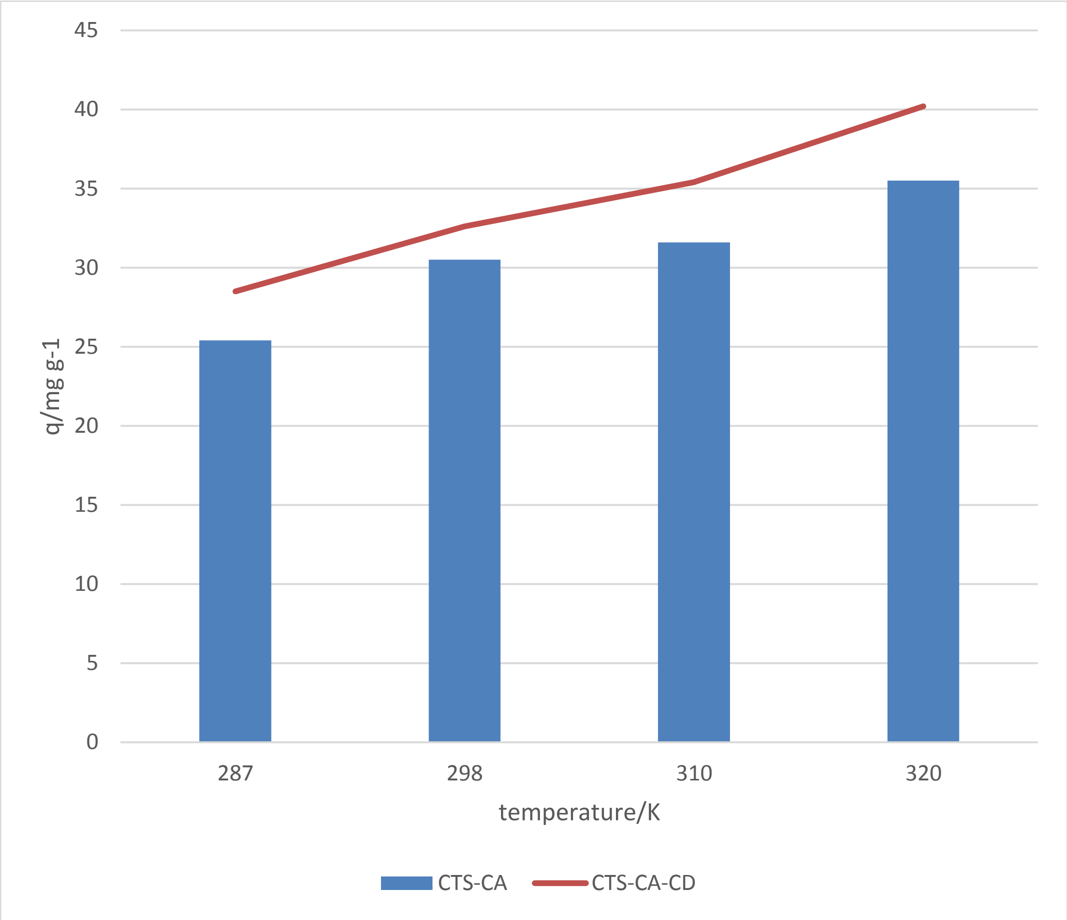

Figure 2. Effect of temperature on adsorption performance

When the temperature of the reaction solution increases, the motion of Ni^{2+} adsorbed on the surface of modified chitosan is accelerated, which increases the contact chance between the adsorption sites on the modified chitosan and Ni^{2+}, so that the original unadsorbed Ni^{2+} is re-adsorbed on the surface of the modified chitosan. site, thus increasing the adsorption capacity.

4.3. Thermodynamics of Adsorption Process

Under the conditions of temperature of 287K, 298K, 310K and 320K, plotting with lnD as the ordinate and 1/T as the abscissa, the results are shown in Figure 3, H and S can be directly obtained from the slope and intercept of the straight line out.

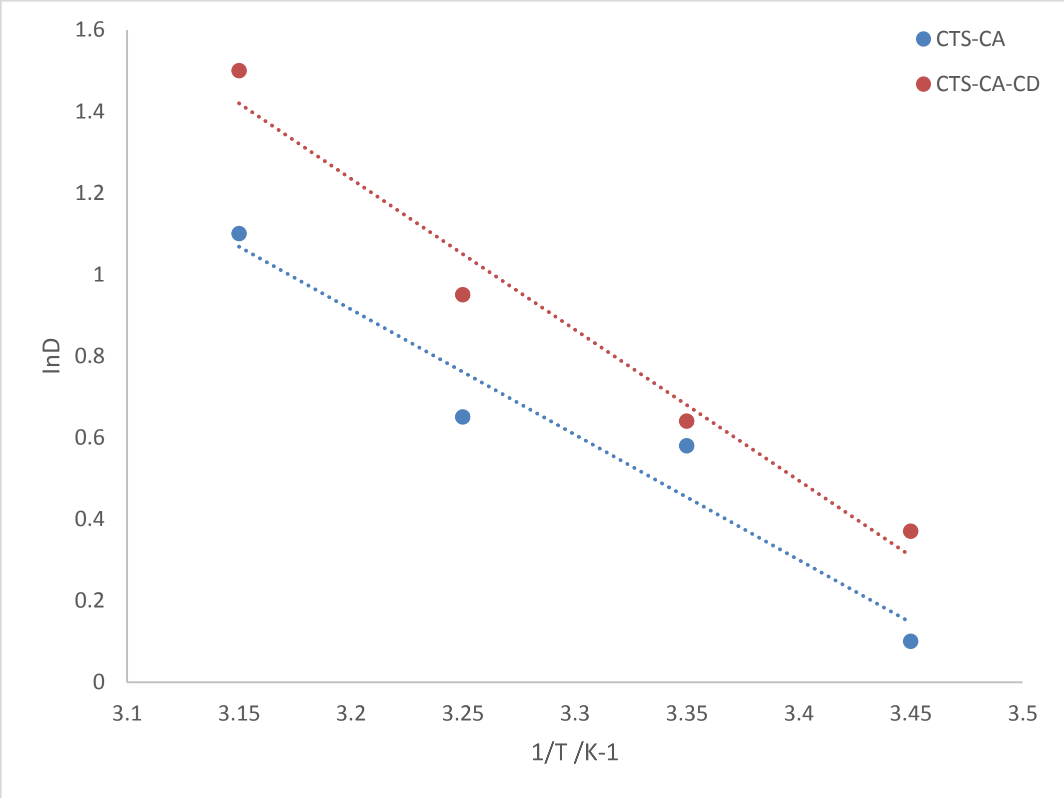

Figure 3. 1nD-1/T linear fitting diagram

According to the curve and formula obtained by fitting in Fig. 3, the enthalpy change ΔH and the entropy change ΔS in the process of adsorbing heavy metal Ni^{2+} by modified chitosan CTS-CA-CD are 23.45kJ/mol and 82.36J/(mo1·K). The enthalpy change ΔH of the modified chitosan CTS-CA-CD during the adsorption of heavy metal Ni^{2+} was 28.64 kJ/mol, and the entropy change ΔS was 101.24 J/(mol·K). Then calculate the Gibbs free energy ΔG at the temperature of 287K, 298K, 310K and 320K by the formula. Its adsorption thermodynamic parameters are shown in Table 2.

Table 2. Thermodynamic parameters of modified chitosan for Nit adsorption

Modified Chitosan	ΔS/[J/(mol K)]	ΔH/(kJ/mol)	ΔG			
			287K	298K	310K	320K
CTS-CA	84.60	23.58	-0.15	-1.05	-1.89	-2.67
CTS-CA-CD	103.45	29.32	-0.56	-1.56	-2.56	-3.64

From the calculation results in Table 2, it can be seen that the enthalpy change ΔH in the adsorption process of Ni^{2+} by the two modified chitosans is greater than 0, indicating that the adsorption process of the two modified chitosans on Ni^{2+} is an endothermic process, and the increase The temperature is favorable for the adsorption of Ni^{2+} on modified chitosan; the entropy change ΔS of the two modified chitosans for the adsorption of Ni^{2+} is greater than 0, indicating that the adsorption process is a process of increasing entropy. It can also be seen from the table that the Gibbs free energy ΔG at the four temperatures is less than 0, indicating that the adsorption of Ni^{2+} by the two modified chitosans can proceed spontaneously. In addition, with the increase of temperature, the corresponding ΔG decreases, which also shows that the increase of temperature is beneficial to the adsorption of Ni^{2+} by the two modified chitosans.

5.Conclusion

In this paper, acrylic acid-modified chitosan magnetic adsorption material was prepared, the effect of the amount of each reagent added on the adsorption performance of the material was systematically analyzed by orthogonal experiments, and the material was characterized and adsorption experiments were carried out. The reasons for the enhanced adsorption performance after material modification were initially explored, and the adsorption mechanism of heavy metals was explained to some extent, which provided valuable data on the adsorption of Pb, Cd and Cu by modified chitosan, and the material could be continuously synthesized. No need to separate intermediate products, which is innovative. Compared with the traditional adsorption materials, the acrylic modified chitosan magnetic adsorption material is easier to separate from the water body after adsorption; it has a high adsorption capacity for heavy metals, and the adsorption material can be reused; it has better performance in the treatment of heavy metal pollution in water bodies. Practical significance and practical value.

Funding

This article is not supported by any foundation.

Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

References

[1] Moon C, Ahn Y, Lee T J, et al. Importance of microbial adaptation for concentrate management in wastewater reuse process:. Energy & Environment, 2019, 30(4):719-731. https://doi.org/10.1177/0958305X18802910

[2] Mian M M, Liu G, Fu B. Conversion of sewage sludge into environmental catalyst and microbial fuel cell electrode material: A review. Science of The Total Environment, 2019, 666(MAY 20):525-539.

[3] Sauperl O, Zemljic L F, Valh J V, et al. Assessment of chemically and enzymatically modified chitosan with eugenol as a coating for viscose functionalization for potential medical use:. Textile Research Journal, 2021, 91(23-24):2813-2832. https://doi.org/10.1177/00405175211021446

[4] Shahraki Z M, Mao X, Waugh S, et al. Potential release of legacy nitrogen from soil

surrounding onsite wastewater leaching pools. Water Research, 2020, 169(Feb.1):115241.1-115241.11. https://doi.org/10.1016/j.watres.2019.115241

[5] Mullasseri S, Mishra R, Jadav R M, et al. Uranium Sequestration - Using bacteria. Current Science, 2021, 120(1):13-15.

[6] Masao M, Giuseppe G, Chiharu T. Recovery of Calcium Fluoride from Highly Contaminated Fluoric/Hexafluorosilicic Acid Wastewater. Materials Transactions, 2018, 59(2):290-296.

[7] Maia, Tatinclaux, Kyla, et al. Electricity generation from wastewater using a floating air cathode microbial fuel cell - ScienceDirect. Water-Energy Nexus, 2018, 1(2):97-103.

[8] Zamouche-Zerdazi R, Bouteraa M, Hallel S, et al. Desalination and Water Treatment Impact of clear waters parasites on the biological wastewater treatment. Desalination and Water Treatment, 2021, 213(2021):106–116. https://doi.org/10.5004/dwt.2021.26695

[9] Mahmud S, Manzur T, Samrose S, et al. Significance of properly proportioned fly ash based blended cement for sustainable concrete structures of tannery industry. Structures, 2021, 29(3):1898-1910.

[10] Ali I, Peng C, Khan Z M, et al. Overview of microbes based fabricated biogenic nanoparticles for water and wastewater treatment. Journal of Environmental Management, 2019, 230(JAN.15):128-150. https://doi.org/10.1016/j.jenvman.2018.09.073

[11] Pfluger A, Hahn M, Hering A, et al. Statistical Exposé of a Multiple-Compartment Anaerobic Reactor Treating Domestic Wastewater.. Water environment research : a research publication of the Water Environment Federation, 2018, 90(6):530-542.

[12] Apichaya, Aneksampant, Kazunori, et al. Microbial Leaching of Iron from Hematite: Direct or Indirect Elution. Materials Transactions, 2020, 61(2):396-401.

[13] Almekhlafi M, Iskandar H G, Zain A, et al. An Optimized Design of Antenna Arrays for the Smart Antenna Systems. Computers, Materials and Continua, 2021, 69(1):1979-1994. https://doi.org/10.32604/cmc.2021.018390

[14] Spro O C, Lefranc P, Park S, et al. Optimized Design of Multi-MHz Frequency Isolated Auxiliary Power Supply for Gate Drivers in Medium-Voltage Converters. IEEE Transactions on Power Electronics, 2020, PP(99):1-1.

[15] Seo Y, Kwon K W. Area-optimized design of SOT-MRAM. IEICE Electronics Express, 2020, 17(21):20200314-20200314. https://doi.org/10.1587/elex.17.20200314

[16] Paeng J, Oh J, Moon K, et al. Optimized Design for Precast L-Type Roadway Gutter Using Modified Sulfur Cement Concrete and Wedge Anchors. Journal of the Korean Society for Advanced Composite Structures, 2020, 11(5):28-33. https://doi.org/10.11004/kosacs.2020.11.5.028

[17] Ahmed S, Emadi H, Heinze L, et al. An Experimental Comparison Between Actual Valve and Benchmark Valve Using Modified Design and Optimized Design. International Journal of Engineering Trends and Technology, 2020, 68(2):64-73. https://doi.org/10.14445/22315381/IJETT-V68I2P212

[18] Das N, Ropmay G D, Joseph A M, et al. Modelling the Effective Conductance Drop due to a Particle in a Solid State Nanopore Towards Optimized Design. IEEE Transactions on NanoBioscience, 2020, PP(99):1-1.