

**Original Article**



# Pectin-Functionalized Magnetic Nanoadsorbent for Efficient Mn<sup>2+</sup> Removal and Reuse

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## Abstract:

To address the environmental pollution caused by Mn<sup>2+</sup>-containing industrial wastewater, this study successfully synthesized a novel, efficient, and magnetically separable composite adsorbent by immobilizing natural biomass pectin onto the surface of aminated core-shell magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@NH<sub>2</sub>). This study systematically investigated the adsorption behavior and desorption-regeneration performance of this material for Mn<sup>2+</sup> in wastewater, aiming to provide theoretical and experimental basis for its practical application.

The composite magnetic nanocomposite adsorbent exhibited excellent Mn<sup>2+</sup> adsorption performance under optimal conditions (dosage 10.0 mg, adsorption time 6.0 h, solution pH 6.0). In 20.0 mL of 100.0 mg/L Mn<sup>2+</sup> solution, its removal efficiency reached 78.02%, and the equilibrium adsorption capacity was as high as 156.03 mg/g. Furthermore, the adsorbent demonstrated outstanding reusability, with a desorption efficiency of 90.04% in the first cycle, highlighting its great potential for practical applications.

**Keywords:** Pectin, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@NH<sub>2</sub>, Composite nano-magnetic adsorbent, Mn<sup>2+</sup> solution, Adsorption-regeneration

## 1. Research Background

In recent years, the presence of "green" technologies has been increasing: electric vehicles (EVs) drive by silently on the roads, and an increasing number of charging stations are being installed in residential areas. New energy vehicles (NEVs) are integrating into my daily life at an unprecedented speed. However, a critical issue closely related to daily living has also emerged: the ultimate fate of the batteries from these EVs after they are retired (or decommissioned). Literature and media reports indicate that if these spent batteries are not handled properly, the internal electrolytes and chemicals may leak, causing contamination to water, air, and soil. Significantly, they contain substantial quantities of valuable heavy metals such as nickel, cobalt, and manganese. If disposed of improperly, this

would constitute a significant waste of resources. This issue, stemming from real-life observations, inspired my interest in inquiry.

Among these heavy metals, manganese (Mn) warrants particular attention. Although manganese is an essential trace element for maintaining normal physiological functions, excessive exposure induces toxicity. Chronic or excessive exposure to manganese may cause initial symptoms such as dizziness and fatigue, in severe cases, it may lead to neurological disorders resembling Parkinson's disease (manganism) [1-3]. Additionally, manganese is the fourth most widely used metal in industry. Its applications are extensive, including the production of glass, ceramics, adhesives, welding materials, paints, gasoline anti-knock additives, and batteries.

Therefore, developing cost-effective technologies to treat Mn-containing industrial wastewater is not only vital for resource recovery but also critical for safeguarding public health.

Currently, conventional technologies for treating heavy metal wastewater include chemical precipitation, physical adsorption, and biological methods [4]. Among them, adsorption is favored for its simplicity, cost-effectiveness, and high efficiency. The efficacy of this technology relies on the availability of high-performance material. However, traditional adsorbents such as activated carbon and zeolites generally suffer from limitations such as low adsorption capacity and challenging recovery and regeneration. Many novel adsorbents reported in recent years are hindered by complex synthesis processes, high costs, or unsatisfactory performance, limiting their potential for large-scale industrial application. Therefore, developing novel adsorbent that are abundant, low-cost, environmentally friendly, and highly efficient remains a primary research focus and difficulty.

Among various candidate materials, pectin has emerged as a promising biomass adsorbent. Primarily, pectin offers distinct environmental and economic advantages. As a ubiquitous polysaccharide found in plant cell walls—particularly in agricultural by-products such as citrus peels and apple pomace—pectin is widely available, cost-effective, and biodegradable. Structurally, pectin possesses inherent properties that make it an effective adsorbent. Its polymeric chain is abundant in active functional groups, specifically carboxyl (-COOH) and hydroxyl (-OH) groups. These functional groups facilitate the effective binding of heavy metal ions from aqueous solutions via electrostatic attraction and chelation mechanisms [5-7]. However, native pectin is subject to limitations, including high water

solubility, poor mechanical strength, and challenges in post-adsorption separation and recovery. While pectin effectively complexes metal ions, integrating it with magnetic materials significantly enhances its adsorption efficiency and separability. Therefore, the inherent limitations of pectin can be overcome by developing composite materials that leverage the synergistic properties of their components.

To address the aforementioned limitations of pectin, this study proposes innovative solution: fabricating a composite of pectin and magnetic nanoparticles [8-10].  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$  was selected as the magnetic core to enable rapid separation and recovery under an external magnetic field, effectively overcoming the challenge of pectin retrieval. By immobilizing pectin onto the surface of the magnetic core, the objective was to synthesize a novel composite material that synergizes the advantages of both components: utilizing the abundant adsorption sites of pectin for efficient  $\text{Mn}^{2+}$  removal, and leveraging the magnetic core for convenient separation and recycling. While magnetic pectin composites have been successfully applied to the adsorption of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  in previous studies [11-13], the novelty of this work lies in the systematic application of this technology to the specific environmental challenge of  $\text{Mn}^{2+}$  pollution derived from spent lithium batteries. This study aims to experimentally validate this concept and provide a promising technical solution for resource recovery.

## 2. Research Process

### 2.1 Materials and Equipment

#### 2.1.1 Materials and Reagents

The main chemical reagents used in this study are shown in Table 2-1.

**Table 2-1 Main Experimental Materials**

Name	Specification	Source Manufacturer
Low-ester Pectin	Food Grade	Xinjiang Fufeng Biotechnology Co., Ltd.
0.1M Sodium Hydroxide	AR	Fludau

Aminated Silica-coated Magnetic Beads	100nm	Jiangsu Zhichuan Technology
Calcium Chloride	AR	Sinopharm Reagent
Anhydrous Sodium Carbonate	AR	Shanghai Zhanyun Chemical Co., Ltd.
Sodium Dodecylbenzenesulfonate	AR	Sinopharm Reagent
Manganese Chloride	AR	damas-beta
Sodium Hydroxide	AR	Sinopharm Reagent
Hydrochloric Acid	AR	Sinopharm Reagent

### 2.1.2 Instruments and Equipment

study are shown in Table 2-2.

The main instruments and equipment used in this

**Table 2-2 Main Instruments and Equipment**

Name	Model	Brand
Analytical Balance	BSA224S	Shanghai Lichen Instrument Co., Ltd.
Magnetic Stirrer	MS3	JOANLAB
Ultrasonic Cleaner	SB-120D	Ningbo Xinzhi Biotechnology Co., Ltd.
Magnet	30mm×5mm	Cilibao
Vacuum Drying Oven	DZF-6090	Shanghai Yiheng Scientific Instrument Co., Ltd.
pH Meter	100pro	Shanghai Lichen Instrument Co., Ltd.
Water Bath Constant Temperature Shaker	DKZ-2B	Shanghai Jinghong Experimental Equipment Co., Ltd.
Fourier Transform Infrared Spectrometer	Nicolet iS20	Thermo Fisher Scientific
Scanning Electron Microscope (SEM)	ZEISS Sigma 300	ZEISS
Nanoparticle and Zeta Potential Analyzer	Nano ZS90	Malvern (UK)
Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)	Avio	PerkinElmer

## 2.2 Experimental Process

### 2.2.1 Preparation of Composite Nano-magnetic Adsorbent

(1) Pretreatment of Pectin Solution (Saponification): First, a pivotal pretreatment step—saponification—was performed on the pectin raw material. Low-ester pectin (1.0 g) was dissolved in 60 mL of 0.1 M NaOH solution and reacted under rapid stirring at 50°C for 1 h. The objective of this saponification was to hydrolyze methyl ester groups (-COOCH<sub>3</sub>) in the pectin molecules under alkaline conditions, thereby exposing

more active carboxyl groups (-COO<sup>-</sup>). These groups serve as key binding sites for the subsequent adsorption of metal ions. Throughout the process, nitrogen gas was introduced to create an inert atmosphere, as polysaccharides are susceptible to oxidative degradation under thermal and alkaline conditions. This nitrogen protection effectively prevented oxidation, thereby maintaining the integrity of the molecular structure.

(2) Dispersion of Magnetic Particles: Aminated silica-coated magnetic particles (1.0 g) were weighed and ultrasonically dispersed in

ultrapure water to prevent aggregation.

- (3) **Cross-linking and Compositing:** Subsequently, the two solutions were mixed and ultrasonicated again to ensure uniform dispersion. A CaCl<sub>2</sub> solution was then added dropwise in a water bath at 40–60°C. The Ca<sup>2+</sup> ions acted as a cross-linking agent. These ions simultaneously bind to -COO<sup>-</sup> groups on adjacent pectin chains, forming stable "egg-box" structures (ionic bridges). This process immobilized the pectin network onto the surface of the magnetic particles, yielding a structurally stable composite material.
- (4) **Post-treatment:** After the reaction, the product was magnetically separated, washed repeatedly with distilled water until neutral, vacuum-dried at 50°C, ground, and stored for further use. Notably, during the initial preparation, the high viscosity of the saponified pectin solution caused aggregation, posing a challenge to uniform mixing. This issue was resolved by optimizing the stirring rate and enhancing the ultrasonic dispersion, thereby ensuring the uniformity of the product.

### 2.2.2 Characterization of Composite Nano-magnetic Adsorbent

- (1) **Fourier Transform Infrared Spectroscopy (FT-IR):** This technique was employed to identify the surface chemical functional groups, confirming the successful grafting of pectin

onto the magnetic particles.

- (2) **Scanning Electron Microscopy (SEM):** SEM was utilized to characterize the microscopic morphology of the material, specifically to assess surface roughness and porosity, which correlate with the abundance of adsorption sites.
- (3) **Zeta Potential Analysis:** This analysis was conducted to measure the surface charge under varying pH conditions, thereby elucidating the mechanism of electrostatic interaction between the material and ions.

### 2.2.3 Mn<sup>2+</sup> Adsorption Experiment

To determine the optimal adsorption conditions, an L9(3<sup>3</sup>) orthogonal array design was employed in this study. Three key factors were investigated: adsorbent dosage (A), adsorption time (B), and initial solution pH (C). The specific levels for each factor are listed in Table 2-3. All adsorption experiments were conducted using 20 mL of Mn<sup>2+</sup> solution (100 mg/L) and agitated at 150 rpm in a constant-temperature water bath shaker. Following adsorption, the adsorbent was magnetically separated, and the residual Mn<sup>2+</sup> concentration in the supernatant was quantified using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The optimal adsorption parameter combination was determined using the removal efficiency and adsorption capacity as evaluation indicators.

**Table 2-3 Orthogonal Experiment Design Table**

Experimental Level	A Dosage / mg	B Time / h	C pH
1	10.0	2.0	4.0
2	15.0	4.0	6.0
3	20.0	6.0	8.0

### 2.2.4 Mn<sup>2+</sup> Desorption and Regeneration Experiment

To evaluate the reusability of the adsorbent,

desorption and regeneration experiments were conducted. In initial attempts, the regeneration efficiency was suboptimal, and the desorption efficiency was very low, raising concerns

regarding the stability of the material. It was hypothesized that the poor performance resulted from an improper selection of the eluent or insufficient contact time. Consequently, different concentrations of EDTA solution were systematically evaluated as the eluent. EDTA can form stable complexes with  $Mn^{2+}$ , theoretically allowing it to sequester  $Mn^{2+}$  from the adsorbent via competitive chelation. Through comparative experiments (specific results in section 3.5), optimal elution conditions were established. Subsequently, multiple "adsorption-desorption" cycles were performed under these conditions to comprehensively evaluate its regeneration performance.

## 2.3 Calculation of Adsorption and Regeneration Function Indicators

### (1) Adsorption Performance Indicators

The removal efficiency and equilibrium adsorption capacity of the adsorbent for  $Mn^{2+}$  were calculated by formulas (1) and (2), respectively:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Where  $C_0$  represents the initial concentration of  $Mn^{2+}$  (mg/L);  $C_e$  denotes the equilibrium concentration of  $Mn^{2+}$  (mg/L).

$$Q_e(\text{mg/g}) = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $V$  is the volume of the solution (L), and  $m$  is the mass of the adsorbent (g).

### (2) Regeneration Performance Indicator

The desorption efficiency was calculated using Equation (3) :

$$D(\%) = \frac{C_d \times V_d}{(C_0 - C_e) \times V} \times 100 \quad (3)$$

Where  $C_d$  is the concentration of  $Mn^{2+}$  in the eluent (mg/L), and  $V_d$  is the volume of the eluent (L). ( $C_0$  and  $C_e$  are defined as above).

## 3 Results and Discussion

### 3.1 Fourier Transform Infrared Spectroscopy Characterization

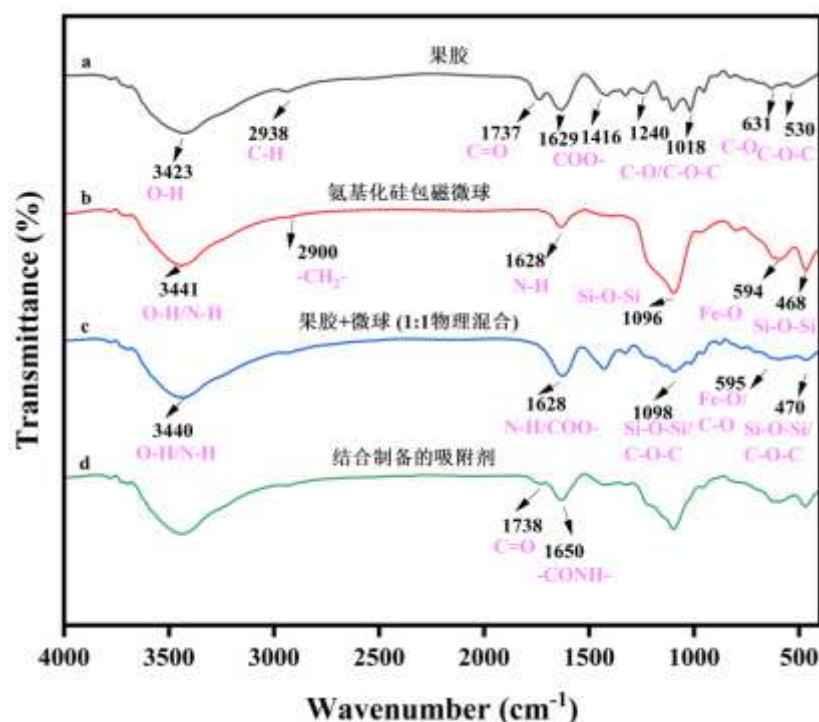
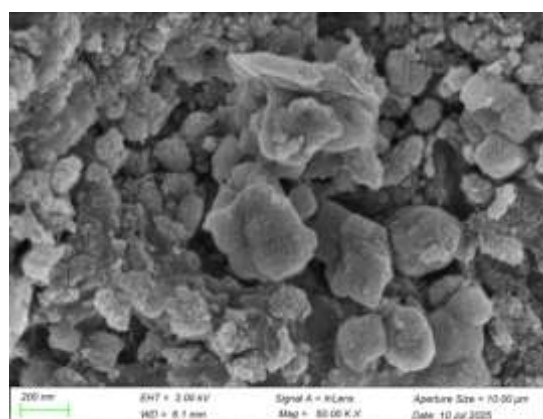
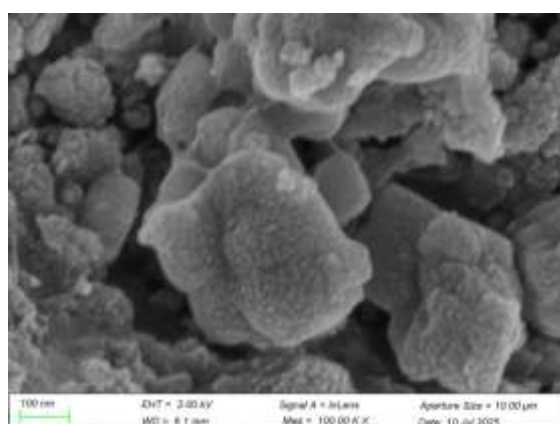


Figure 3-1 FT-IR spectra of different materials

To verify the successful synthesis of magnetic nanocomposite adsorbent, the raw materials (pectin, aminated silica-coated magnetic beads), their physical mixture, and the final product were characterized using FT-IR (Figure 3-1). Curve a shows the spectrum of pure low-ester pectin. Typical polysaccharide broad absorption peaks typical of polysaccharides were observed at  $\sim 3423\text{ cm}^{-1}$  (O-H stretching vibration) and  $\sim 2938\text{ cm}^{-1}$  (C-H stretching vibrations), along with complex C-O-C and C-O vibration peaks in the fingerprint region ( $1000\text{--}1200\text{ cm}^{-1}$ ). The sharp absorption peak at  $1737\text{ cm}^{-1}$  is attributed to the C=O stretching vibration of esterified carboxyl groups ( $-\text{COOCH}_3$ ), while the absorption peaks at  $1629\text{ cm}^{-1}$  and  $1416\text{ cm}^{-1}$  correspond to the asymmetric and symmetric stretching vibrations of free carboxyl groups ( $-\text{COO}^-$ ), respectively. Curve b represents the spectrum of the aminated silica-coated magnetic nanoparticles. Strong absorption peaks at  $\sim 594\text{ cm}^{-1}$  and  $\sim 468\text{ cm}^{-1}$  correspond to the vibrations of Fe-O bonds and Si-O-Si bonds, respectively, confirming the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core structure. The Si-O-Si asymmetric stretching vibration peak at  $\sim 1096\text{ cm}^{-1}$  further confirms the presence of the silica

coating. The absorption peak at  $\sim 1628\text{ cm}^{-1}$  is assigned to the N-H bending vibration, indicating the successful surface amination. Curve c displays the spectrum of the physical mixture of pectin and magnetic nanoparticles. This spectrum is basically a simple linear superposition of the characteristic peaks of the two, and no new chemical bonds were observed. Conversely, in the spectrum of final composite adsorbent (Curve d), the most significant change is the appearance of a new shoulder peak at  $\sim 1650\text{ cm}^{-1}$ . Located between the  $-\text{COO}^-$  asymmetric stretching vibration of pectin and the N-H bending vibration of the amino group, this peak is assigned to the C=O stretching vibration (amide I band) in the newly formed amide bond ( $-\text{CONH}-$ ). The formation of this new chemical bond provides direct evidence of the condensation reaction between the carboxyl groups on the pectin molecular chain and the amino groups on the surface of the magnetic particles. This confirms that the pectin was successfully grafted onto the surface of the magnetic particles via covalent bonding, rather than simple physical adsorption.

### 3.2 SEM Characterization



**Figure 3-2 SEM images of composite nano-magnetic material**

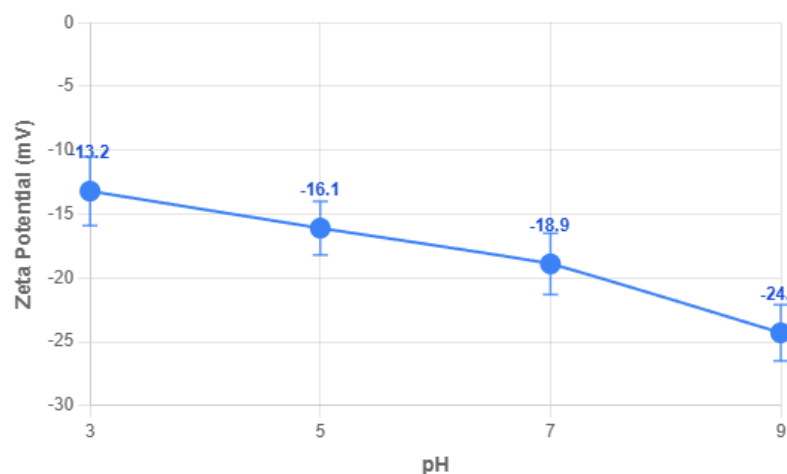
The surface morphology of the magnetic nanocomposite adsorbent was characterized via SEM (Figure 3-2). Low- and high-magnification images reveal that the synthesized particles exist as near-spherical aggregates with relatively

uniform size distributions. Rather than exhibiting a smooth surface, the particles display a highly rough and uneven texture characterized by abundant folds, grooves, and micropores. This complex three-dimensional porous architecture

significantly enhances the effective specific surface area, thereby increasing the availability of active sites for the subsequent adsorption process. This unique surface structure is the structural

foundation for high-efficiency adsorption, indicating the material's promising potential for practical applications.

### 3.3 Zeta Potential Characterization



**Figure 3-3 Zeta potential of adsorbent at different pH conditions**

To investigate the influence of pH value on the surface charge properties of the adsorbent, Zeta potential measurements were conducted. The adsorbent was ultrasonically dispersed into a series of buffer solutions (pH 3.0, 5.0, 7.0, and 9.0) to obtain uniform suspensions. Samples were subsequently analyzed using a nanoparticle and Zeta potential analyzer, with results shown in Figure 3-3. The results show that within the investigated pH range, the material surface remained negatively charged, with Zeta potential values decreasing (becoming more negative) as pH increased. This trend is attributed to the deprotonation of abundant acidic functional groups (mainly  $-\text{COO}^-$ ) on the material surface at higher pH levels. These groups facilitate the capture of positively charged  $\text{Mn}^{2+}$  ions via strong electrostatic attraction. Mechanistically, this

implies that higher pH conditions favor adsorption. However, determining the optimal pH requires balancing surface charge with metal ion speciation to prevent  $\text{Mn}(\text{OH})_2$  precipitation at excessively high pH, which could confound adsorption results.

### 3.4 Orthogonal Experiment

#### 3.4.1 Analysis of Orthogonal Experiment Adsorption Rate under Different Adsorption Conditions

To systematically optimize the adsorption process parameters, the study used the  $L_9(3^3)$  orthogonal experiment method to investigate three key factors: adsorbent dosage, adsorption time, and solution pH.

**Table 3-1 Visual Analysis of Orthogonal Experiment Adsorption Rate**

Exp. No.	A	B	C	Adsorption Rate/%
1	10.0	2.0	4.0	69.48
2	10.0	4.0	8.0	59.78
3	10.0	6.0	6.0	79.76
4	15.0	2.0	8.0	61.44

5	15.0	4.0	6.0	86.23
6	15.0	6.0	4.0	69.93
7	20.0	2.0	6.0	81.17
8	20.0	4.0	4.0	71.33
9	20.0	6.0	8.0	63.73
K <sub>1</sub>	69.7	70.7	70.2	—
K <sub>2</sub>	72.5	72.4	82.4	—
K <sub>3</sub>	72.1	71.1	61.7	—
R	2.9	1.7	20.7	—
Order of Influence	pH > Dosage > Time			
Optimal Combination	Dosage 15.0mg, Time 4.0h, pH 6.0 (A <sub>2</sub> B <sub>2</sub> C <sub>2</sub> )			

When using adsorption rate as the evaluation criterion, magnitude of influence of each factor was evaluated based on the range (R).. As presented in Table 3-1,  $R(\text{pH}) = 20.7 \gg R(\text{Dosage}) = 2.9 > R(\text{Time}) = 1.7$ , indicating that the solution pH was the most significant factor affecting the  $\text{Mn}^{2+}$  adsorption rate, followed by dosage, while time exerted the minimal influence. This finding aligns with the analysis results of the

Zeta potential in section 3.3, i.e., a higher pH (pH 6.0,  $K_2=82.4$ ) can provide a stronger driving force for electrostatic attraction. Based on the K value analysis, the theoretical optimal combination was determined to be A<sub>2</sub>B<sub>2</sub>C<sub>2</sub>.

### 3.4.2 Analysis of Orthogonal Experiment Unit Adsorption Capacity under Different Adsorption Conditions

**Table 3-2 Visual Analysis of Orthogonal Experiment Adsorption Capacity**

Exp. No.	A	B	C	Adsorption Capacity mg/g
1	10.0	2.0	4.0	138.96
2	10.0	4.0	8.0	119.56
3	10.0	6.0	6.0	159.52
4	15.0	2.0	8.0	81.92
5	15.0	4.0	6.0	114.97
6	15.0	6.0	4.0	93.24
7	20.0	2.0	6.0	81.17
8	20.0	4.0	4.0	71.33
9	20.0	6.0	8.0	63.73
K <sub>1</sub>	139.3	100.7	101.2	—
K <sub>2</sub>	96.7	102.0	118.6	—
K <sub>3</sub>	72.1	105.5	88.4	—
R	67.3	4.8	30.1	—
Order of Influence	Dosage > pH > Time			
Optimal Combination	Dosage 10.0mg, Time 6.0h, pH 6.0 (A <sub>1</sub> B <sub>3</sub> C <sub>2</sub> )			

Conversely,, when using unit adsorption capacity served as the evaluation criterion, the hierarchy of influence of the factors shifted. As shown in Table 3-2,  $R(\text{Dosage}) = 67.3 \gg R(\text{pH}) = 30.1 > R(\text{Time}) = 4.8$ , indicating that the adsorbent dosage becomes the most critical factor affecting

the adsorption capacity. This is because, with a fixed total amount of  $\text{Mn}^{2+}$ , increasing the adsorbent dosage enhances the total removal rate, but reduces the mass of  $\text{Mn}^{2+}$  adsorbed per unit mass of adsorbent, thus lowering the unit adsorption capacity. Based on the K value analysis, the theoretical optimal combination for

maximizing adsorption capacity was determined to be  $A_1B_3C_2$ .

### 3.4.3 Orthogonal Experiment Verification Experiment

**Table 3-3 Orthogonal Experiment Verification Experiment**

Condition Combination	Adsorption Rate %	Adsorption Capacity mg/g
$A_2B_2C_2$	85.69	114.25
$A_1B_3C_2$	78.02	156.03

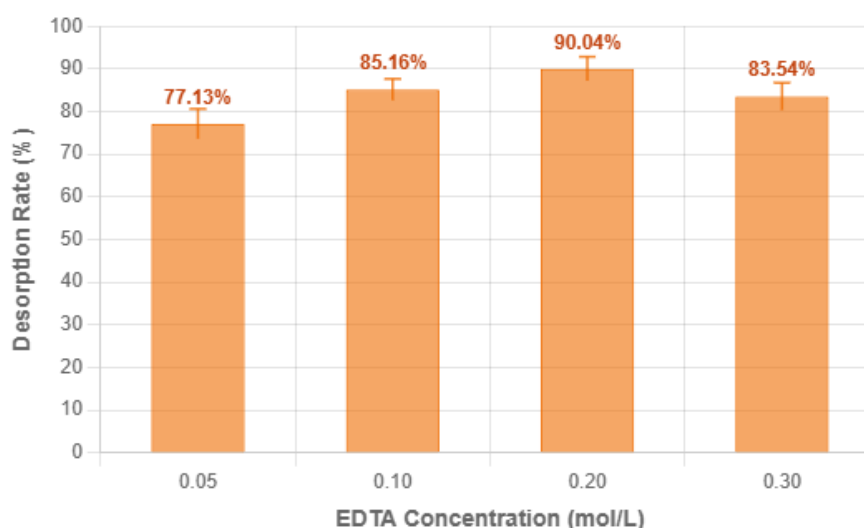
To identify the optimal experimental conditions, verification experiments were conducted on the two theoretical combinations (Table 3-3). Results indicate that while  $A_2B_2C_2$  combination could indeed achieve a higher removal rate, but its unit adsorption capacity was substantially lower than that of the  $A_1B_3C_2$ . In evaluating adsorbent performance, unit adsorption capacity is considered a superior indicator of intrinsic efficiency and economic viability. Therefore, to maximize material utilization while ensuring a high removal rate (78.02%),  $A_1B_3C_2$  (Dosage: 10.0 mg; Time: 6.0 h; pH: 6.0) was ultimately established as the optimal adsorption condition. To objectively assess the performance of this adsorbent, its maximum adsorption capacity (156.03 mg/g) was compared with literature values for other adsorbents. It was found to be superior to common materials such as biochar and modified clay minerals. These comparative results demonstrate that the synthesized material possesses significant competitive advantages and

promising application prospects for treating Mn-containing wastewater.

### 3.5 Desorption and Regeneration Experiment

#### 3.5.1 Selection of Desorption Conditions

The economic viability and environmental sustainability of an adsorbent hinge on its effective regeneration and reusability. EDTA was selected as the eluent due to its strong chelating affinity for divalent metal ions. Figure 3-4 shows the desorption efficiency using varying concentrations of EDTA on  $Mn^{2+}$ . The desorption efficiency initially increased with EDTA concentration, peaking at 90.04% at 0.20M, before slightly declining. This indicates that this concentration of EDTA can effectively elute the adsorbed  $Mn^{2+}$  from the material surface, thereby facilitating the regeneration of the adsorbent. Consequently, 0.20M was identified as the optimal desorption agent concentration for subsequent cycle experiments.



### Figure 3-4 Adsorbent desorption effect at different EDTA concentrations

#### 3.5.2 Cyclic Regeneration Experiment

The reusability of the adsorbent was investigated under optimal adsorption and desorption conditions (Figure 3-5). The results show that the composite adsorbent has favorable regeneration performance. In the first cycle, both the adsorption rate and desorption rate were excellent. However, as the cycle count reached four, both efficiencies exhibited a notable decline. The adsorption rate could remain at 62.44% after

the second cycle, indicating moderate stability. The performance decline is likely attributed to the partial degradation or leaching of active components (such as pectin) from the material surface, as well as the irreversible occupation or blockage of some adsorption sites during repeated cycling <sup>1</sup>Error! Reference source not found. Despite the decline, the adsorbent retained considerable adsorption-desorption capability, underscoring its potential as a reusable adsorbent for practical applications.

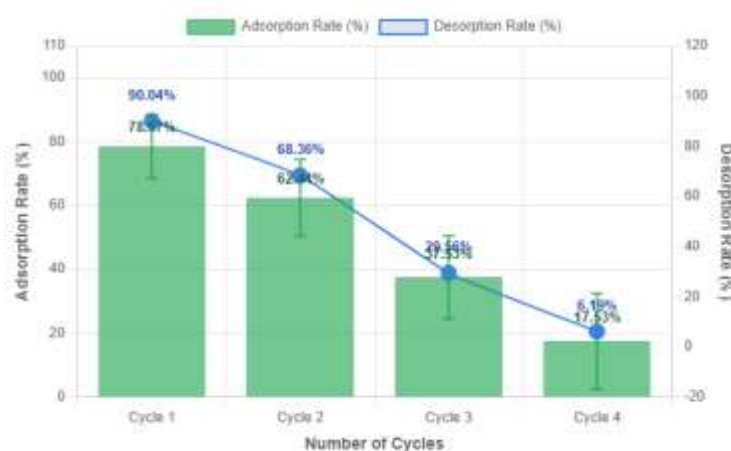


Figure 3-5 Adsorbent desorption effect at different cycle numbers

#### 4 Conclusion and Outlook

This study successfully synthesized a pectin-functionalized core-shell magnetic nanocomposite adsorbent and systematically evaluated its  $Mn^{2+}$  adsorption behavior and regeneration performance. This work provides an efficient and eco-friendly strategy for treating heavy metal industrial wastewater. The main conclusions are as follows:

(1) Characterization via FT-IR and SEM confirmed that pectin was successfully grafted onto the surface of the aminated silica-coated  $Fe_3O_4$  magnetic core via covalent bonds. The resulting core-shell composite exhibited a rough, porous morphology with a high specific surface area.

- (2) Orthogonal experimental results indicated that under the optimal process parameters (adsorbent dosage 10.0 mg, adsorption time 6.0 h, initial solution pH 6.0), the unit adsorption capacity of the adsorbent for  $Mn^{2+}$  was as high as 156.03 mg/g. This performance is significantly superior to that of most biochar and modified clay mineral adsorbents reported in the literature.
- (3) The composite adsorbent exhibited excellent magnetic response and cyclic regeneration capabilities. Considerable adsorption efficiency was retained after four adsorption-desorption cycles, demonstrating its potential for cost-effective practical applications.

While this study demonstrates the application potential of this material, bridging the gap between b

ench-scale research and industrial application requires further investigation in the following areas:

- (1) In-depth analysis and verification of adsorption mechanism: While this study confirmed the role of electrostatic attraction via Zeta potential analysis, specific chemisorption mechanisms, such as complexation or chelation between  $Mn^{2+}$  and the functional groups (e.g.,  $-COO^-$ )—remain to be fully clarified. Future research should integrate adsorption modeling (thermodynamics, kinetics, and isotherms) with advanced spectral techniques, particularly X-ray photoelectron spectroscopy (XPS). These methods will facilitate the identification of atomic-level changes in elemental valence states and chemical environments, ultimately enabling the construction of a comprehensive model synergizing physisorption and chemisorption..
- (2) Study on selective adsorption behavior in complex media: Real-world industrial wastewater (particularly spent battery leachate) often contains a variety of coexisting cations. Coexisting ions (such as  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) inevitably compete for active sites, potentially inhibiting  $Mn^{2+}$  adsorption.. Therefore, conducting multi-component competitive adsorption experiments is crucial for evaluating selectivity and verifying the material's feasibility for precise pollutant removal in complex environments. Furthermore, density functional theory (DFT) calculations should be employed to theoretically quantify interaction energies between metal ions and active sites, providing guidance for targeted material design.
- (3) Exploration of material's macroscopic configuration and engineering application: The current nano-powdered adsorbent may face challenges regarding mass loss during separation and hydraulic issues (e.g., pressure drop) in practical applications. Therefore, immobilizing the nano-adsorbent onto macroscopic carriers (such as hydrogels, porous foams, or fiber membranes) and conducting continuous-flow fixed-bed

column experiments are essential steps toward industrialization. This will help to obtain key parameters necessary for engineering design, such as breakthrough curves and mass transfer zone lengths.

- (4) Life Cycle Assessment (LCA): To ensure sustainability, a comprehensive LCA should be conducted covering the material's entire life cycle—from preparation and application to disposal. This assessment will evaluate environmental impacts and economic costs, providing a scientific basis for developing genuinely green water treatment technologies.

### Acknowledgements

Under the supervision of my advisors, this research was conducted primarily by me over a six-month period. Specifically, I independently executed the synthesis of the magnetic nanocomposite, characterized the material (FT-IR, SEM, Zeta potential), and conducted comprehensive performance testing. This included designing and executing the  $L_9(3^3)$  orthogonal experiment, determining the maximum  $Mn^{2+}$  adsorption capacity, and performing four cyclic regeneration experiments.

During the conceptualization phase, my supervisors provided guidance on establishing the research direction. They offered critical review and suggestions for the experimental design, particularly regarding the orthogonal array. Furthermore, I received training in the operation of precision instruments (ICP and Zeta potential analyzers) and benefited from their academic guidance regarding peak assignments in infrared spectra, specifically for the newly emerged amide/ester peaks. During manuscript preparation, my supervisors provided valuable feedback on the logical flow of the discussion and the overall structure.

Several technical challenges were encountered and resolved during the research. For example, initial experiments revealed that pectin tended to aggregate in alkaline solutions, affecting reaction uniformity. This issue was mitigated by maintaining an

inert nitrogen atmosphere, enhancing agitation, and optimizing water addition. Agglomeration of magnetic nanoparticles in the aqueous phase was overcome by secondary ultrasonication and the addition of sodium dodecylbenzenesulfonate (SDBS) as a dispersant. In regeneration experiments, desorption efficiency initially declined significantly after the first cycle. Following systematic optimization, the use of 0.20 M EDTA combined with optimized elution timing effectively enhanced the cyclic stability.

Through this project, I acquired in-depth knowledge of nanomaterial synthesis, characterization, and environmental applications. More importantly, I honed my skills in independent experimental design, data analysis, and scientific problem-solving. This experience has solidified my interest in scientific research and reinforced my determination to pursue advanced studies in related fields.

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