RESEARCH ARTICLE

Efficient treatment of industrial wastewater using adsorption pretreatment coupled with membrane bioreactor

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Membrane fouling severely limits the application of membrane bioreactors in the treatment of high-strength industrial wastewater. To address this issue, this study focused on the synergistic effect between adsorption pretreatment and the membrane system, designing and constructing an adsorption-coupled aerobic granular sludge membrane bioreactor that utilized iron-based nano-oxides as the pretreatment unit. Meanwhile, the study systematically evaluated the pollutant removal capacity and membrane fouling mitigation effect of iron-based nano-oxide adsorbent in industrial wastewater treatment. A systematic comparison evaluated the removal performance of nano-Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3 at concentrations of 0.5 - 2.0 g/L for key pollutants of total phosphorus (TP), chemical oxygen demand (COD), total nitrogen (TN), suspended solids (SS), and polysaccharides in extracellular polymeric substances. The results demonstrated γ-Fe_2O_3's superior performance, achieving 75.51% COD removal, 97.66% TP removal, and over 44% polysaccharide removal at 2.0 g/L dosage. γ-Fe_2O_3 significantly outperformed Fe_3O_4, α-Fe_2O_3, and conventional granular activated carbon. Further analysis through membrane flux monitoring, Zeta potential, and extended Derjaguin-Landau-Verwey-Overbeek theory showed that the surface electrical properties and particle size characteristics of nanoparticles could remarkably affect pollutant-membrane interfacial interactions. The membrane flux retention rate after γ-Fe_2O_3 treatment was as high as 0.658, which notably inhibited the formation of membrane fouling. Overall, as an adsorption pretreatment material, iron-based nano-oxides could effectively reduce the pollutant load before the membrane, improve interface interaction, and delay membrane fouling, which provided a new strategy for the efficient treatment of high-strength industrial wastewater. Meanwhile, the study offered a theoretical basis and engineering reference for the in-depth coupling of adsorption pretreatment and membrane technology.

Keywords: membrane bioreactor; iron-based nano-oxides; industrial wastewater; pollutant removal; membrane fouling mitigation; aerobic granular sludge.

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Introduction

With the continuous advancement of global industrialization, the sustainable management of industrial wastewater has become a critical issue in the field of environmental engineering. Membrane bioreactor (MBR) technology, owing to its exceptional pollutant retention capacity, is regarded as an important means to achieve efficient industrial wastewater treatment [1]. As a reliable and mature technology, MBR exhibits significant advantages in reducing footprint and improving effluent quality [2]. However, when confronted with the increasingly complex composition of pollutants in urban water systems, traditional membrane technologies still face technical limitations in removing emerging contaminants [3]. Particularly in developing countries, despite the substantial application potential of MBR technology, its widespread adoption is restricted by high operation and maintenance costs [4]. To address this economic and technical bottleneck, global techno-economic analyses indicate that optimizing system configurations to reduce energy consumption is a key direction for enhancing the engineering feasibility of MBR [5].

To overcome the core obstacle of membrane fouling and enhance treatment efficiency, the academic community has conducted a substantial body of targeted cutting-edge research. Egea-Corbacho *et al*. compared advanced MBR technology with conventional processes, confirming the superiority of membrane systems in microplastic removal [6]. Regarding membrane fouling control, Zhang *et al*. reviewed the research progress of electrically enhanced membrane bioreactors (EMBR) and pointed out that an electric field could effectively alleviate membrane pore clogging [7]. Mao *et al*. further optimized the process parameters of an EMBR based on polyvinylidene fluoride, achieving a simultaneous enhancement in treatment performance and anti-fouling properties [8]. Beyond electrochemical assistance, Zhang *et al*. explored the influence of membrane material surface characteristics on the denitrification performance of hydrogen-based membrane biofilm reactors (H_2-MBfRs) [9]. Furthermore, aerobic granular sludge (AGS) has garnered significant attention due to its excellent settling properties. Ahmed *et al*. investigated methods to enhance AGS densification through microbial selection strategies when treating high-strength industrial wastewater [10]. Meanwhile, the introduction of nanomaterials has brought revolutionary breakthroughs to water treatment technology. Kamyab *et al*. explored the application potential of metal and metal oxide nanomaterials in wastewater treatment, emphasizing the contribution of their antimicrobial properties to maintaining system stability [11]. To achieve green synthesis of materials, Alprol *et al*. investigated techniques for biosynthesizing metal oxide nanoparticles using marine algae and validated their application effectiveness in adsorption and photocatalysis [12]. In terms of membrane material modification, Ranjbaran *et al*. fabricated a polysulfone nanocomposite membrane embedded with graphene oxide-decorated copper nanoparticles, which effectively inhibited biofouling during pharmaceutical wastewater treatment [13]. Concerning iron-based adsorbent materials, Onursal elaborated in detail on their high efficiency and cost-effectiveness as adsorbents for removing specific pollutants [14]. Sun *et al*. reviewed the catalytic characteristics and application status of iron-based materials in heterogeneous Fenton oxidation systems [15]. Specifically, regarding magnetic iron oxide nanoparticles, Keshta *et al*. systematically summarized their functionalization strategies and the latest advances in their application for complex wastewater treatment [16]. Coupling efficient adsorption pretreatment with a membrane bioreactor (Adsorption-coupled AGMBR) is considered an effective approach to address the challenges of treating high-strength industrial wastewater. Qin *et al*. analyzed advanced coagulation strategies within AGMBR systems, comparing the effects of various inorganic and modified microbial flocculants on membrane fouling control [17]. Zhang *et al*. introduced a Fe_3S_4/peroxymonosulfate pre-oxidation system and revealed the critical role of pH in enhancing membrane fouling mitigation in AGMBR [18]. Recently, Zhang *et al*. further investigated the impact mechanisms of structural variations in carbon-based adsorbents on AGMBR performance [19]. However, despite these advances, there is still a lack of systematic reports on the performance differences of iron-based nano-oxides with different crystalline structures as pretreatment units in AGMBR. In particular, studies analyzing their anti-fouling mechanisms from the perspective of microinterface energy based on the extended Derjaguin-Landau-Verwey-Overbeek theory remain scarce.

This study aimed to construct a novel adsorption pretreatment-coupled AGMBR system to systematically evaluate the efficacy of different iron-based nano-adsorbents. Three typical materials including nano-Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3 were selected to compare and analyze their removal capabilities for chemical oxygen demand (COD), total phosphorus (TP), and extracellular polymeric substances (EPS) from industrial wastewater. By integrating data on Zeta potential, particle size distribution, and membrane flux variation, this study utilized the extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory to calculate the interaction energy between pollutants and the membrane surface. The results of this study elucidated the microscopic anti-fouling mechanisms of nano-adsorbents, providing a theoretical foundation and technical framework for integrating nanotechnology with membrane systems in high-strength industrial wastewater treatment.

Materials and methods

Construction and operation parameters of the adsorption pretreatment-coupled AGMBR system

The integrated adsorption pretreatment-coupled AGMBR system constructed in this study primarily consisted of a sequencing batch reactor (SBR), a pre-adsorption reactor, and a membrane filtration unit. The custom-made laboratory-scale SBR was fabricated from transparent Plexiglas with a height of 1.0 m, an inner diameter of 0.14 m, an effective volume of 13.2 L, and a designed hydraulic retention time of 4 h. During the pre-adsorption stage, an IKA RCT Basic magnetic stirrer (IKA-Werke GmbH & Co. KG, Staufen, Germany) maintained mixing at 150 rpm to ensure sufficient contact between the adsorbent and the wastewater. The membrane filtration unit utilized a polytetrafluoroethylene microfiltration membrane with diameter of 90 mm, effective area of 36.2 cm^2, average pore size of 0.1 µm (Sigma-Aldrich, St. Louis, MO, USA). The membrane was hydrophilic with a Zeta potential of –33.69 ± 0.10 mV and a contact angle of 52.81 ± 1.56°. Experiments were conducted in dead-end filtration mode with a transmembrane pressure (TMP) of 0.05 MPa provided by high-purity nitrogen. After the SBR completed one operation cycle, some residual pollutants still existed in the effluent and were transferred to the pre-adsorption reactor for further treatment. The adsorption unit had a design capacity of 1 L. Three types of iron-based nano-metal oxide adsorbents including nano-Fe_3O_4, nano-γ-Fe_2O_3, and nano-α-Fe_2O_3 (Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) were added to the reactor to investigate their differential performance in pollutant adsorption and membrane fouling mitigation by using granular activated carbon (GAC) (Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China) as the control. During the reaction, a magnetic stirrer maintained a stirring speed of 150 rpm to ensure uniform contact between nanoparticles and the water body. The adsorbent dosing concentrations were set at 0, 0.5, 1.0, 1.5, and 2.0 g/L with the reaction being conducted at room temperature for 2 hours followed by a 5-minute static settlement. After settlement, 600 mL of supernatant was collected for membrane filtration experiments. Meanwhile, the membrane body was hydrophilic with a Zeta potential of –33.69 ± 0.10 mV, and a water contact angle of 52.81 ± 1.56°. The filtration experiments were performed in a dead-end filtration setup with a single influent volume of 200 mL, and each experiment included three cycles. Dead-end filtration was different from the actual industrial crossflow filtration system. However, this study aimed to preliminarily screen the performance of different nano-adsorbents and analyze the membrane fouling mechanism. Therefore, this facility setting provided a stable and controllable experimental model for comparing the effects of diverse pretreatment methods. During filtration, a TMP of 0.05 MPa was provided by high-purity nitrogen. Hence, the dynamic formation of membrane fouling during operation was realistically reproduced.

Preparation of simulated industrial wastewater

The industrial wastewater used in this research was synthetically prepared with its composition modeled after the organic matter, nitrogen-phosphorus nutrients, and metal ions in typical high-load industrial drainage. The mixed solution consisted of various biodegradable and refractory organic pollutants supplemented with essential nutrients and trace elements to systematically explore the system's removal performance and membrane fouling characteristics. To accurately simulate complex pollution environments, basic inorganic chemicals including sodium acetate ($C_2H_3O_2Na$), ammonium chloride (NH_4Cl), and potassium dihydrogen phosphate (KH_2PO_4) were selected as simulation sources for major pollutants. Polyvalent metal salts including magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and iron (II) sulfate heptahydrate were additionally introduced to mimic the interference of potential bacteriostatic or flocculating ions in industrial wastewater. The final COD was set at 600 mg/L, ammonia nitrogen (NH_4^+–N) was controlled at 60 mg/L, and phosphate (PO_4^{3-}–P) concentration was 6 mg/L. Moreover, magnesium ions (Mg^{2+}) and calcium ions (Ca^{2+}) ($CaCl_2$) were 20 mg/L and 25 mg/L, respectively, and ferrous ions (Fe^{2+}) ($FeSO_4 \cdot 7H_2O$) were set at 10 mg/L. Furthermore, to simulate the potential trace element load in industrial wastewater, a composite trace element solution was added to the system at a dosage of 1 mL/L, which contained 40 mg/L ethylenediaminetetraacetic acid, 100 mg/L $MnCl_2 \cdot 4H_2O$, 73.33 mg/L $NiCl_2 \cdot 6H_2O$, 30 mg/L $CuSO_4 \cdot 5H_2O$, 120 mg/L $ZnSO_4 \cdot 7H_2O$, 360 mg/L $CoCl_2 \cdot 6H_2O$, 100 mg/L H_3BO_3, and 50 mg/L $AlCl_3$. These reagents were used to construct a multi-metal pollution background system highly similar to actual industrial emissions. The simulated wastewater, after treatment by AGS, served as the influent for subsequent adsorption and membrane filtration studies. The aerobic granular sludge used in this study was obtained from the Xin Xinban Wastewater Treatment Plant (Hohhot, Inner Mongolia, China). Following laboratory acclimation, the sludge exhibited a particle size distribution ranging from 0.5 to 4.2 mm with a mixed liquor suspended solids (SS) concentration stably maintained at approximately 4,000 mg/L and a sludge volume index of 44.94 ± 2.54 mL/g, indicating good settling performance and metabolic activity.

The effects of absorbents on representative pollutant indices of industrial wastewater

Experiments were conducted to test pollutant removal efficiency, changes in hydraulic performance, and evolution of particle characteristics. COD, total nitrogen (TN), TP, SS, and polysaccharide/protein contents were quantified as representative pollutant indices of industrial wastewater. COD was measured by potassium dichromate oxidation-spectrophotometry. TN was determined by alkaline potassium persulfate digestion combined with ultraviolet spectrophotometric detection. TP detection relied on the optical absorption of blue complexes produced by ammonium molybdate reduction reaction. SS was obtained by gravimetric drying and weighing. Polysaccharides and proteins in EPS were quantitatively analyzed by phenol-sulfuric acid method and Coomassie Brilliant Blue colorimetric method, respectively. To reveal changes in the interfacial properties of particles during the adsorption process, the Zeta potential of the samples was measured by using a Zetasizer Nano ZS90 analyzer (Malvern Panalytical Ltd., Malvern, Worcestershire, UK). Each sample was measured at least six times to ensure reproducibility. Particle size distribution was determined by using a Mastersizer 3000 laser diffraction particle size analyzer (Malvern Panalytical Ltd., Malvern, Worcestershire, UK), and the volume-weighted mean diameter (D [4, 3]) was obtained. Each group of samples was measured three times, and the average value was calculated. The dynamic changes of membrane properties were analyzed through flux and fouling resistance. The amount of water output per unit membrane area per unit time was defined as the membrane flux (J), which was calculated as follows.

$$J = \frac{V}{t \cdot A} \quad (1)$$

where J was the membrane flux in $L/m^2 \cdot h$. V was the volume of filtrate fluid in L. t was the filtration time in h. A was the effective area of the membrane in m^2.

To clarify the pollutant removal capabilities of different iron-based nano-oxides types in industrial wastewater treatment, four addition concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L, and 2.0 g/L were set for three iron-based nano-metal oxide adsorbents of nano-Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3. Meanwhile, their removal effects on typical pollution factors of COD, TN, TP, SS, and polysaccharides in EPS were systematically compared. The adsorption experiments were conducted under static conditions. The regulatory trends of different particle types and dosages on pollutant removal rates were evaluated by combining changes in water quality parameters before and after adsorption.

Statistical analysis

SPSS Statistics 25.0 (IBM Corp., Armonk, NY, USA) was employed for statistical analysis of the data. Pearson correlation analysis was used to evaluate the correlations between indicators such as COD, polysaccharides, SS, TN, TP, Zeta potential, particle size, and membrane fouling resistance including total resistance (Rt), reversible resistance (Rr), and irreversible resistance (Rir). Correlation coefficients ranged from -1 to 1, and P values less than 0.05 were considered statistically significant.

Results

The treatment efficiency and effluent characteristics of SBR

Monitoring of the SBR effluent quality indicated that the system achieved effective removal of most organic matter and SS, but exhibited limited removal capacity for nitrogen, phosphorus, and extracellular polymers. The influent COD was 680 ± 32 mg/L, which was reduced to 215 ± 18 mg/L after SBR treatment, corresponding to a removal rate of 68.4%. The removal rates for TN and TP were 47.2% (decreasing from 72 ± 4 mg/L to 38 ± 3 mg/L) and 66.7% (decreasing from 12 ± 1 mg/L to 4 ± 0.5 mg/L), respectively. The SS concentration decreased significantly from 180 ± 12 mg/L to 32 ± 5 mg/L, achieving a high removal rate of 82.2%. However, a relatively high concentration of extracellular polysaccharides of 28 ± 2 mg/L with a removal rate of only 37.8% remained in the effluent. If these residual pollutants directly entered the subsequent membrane module, they would readily induce severe membrane fouling. Therefore, the introduction of an adsorption pretreatment unit was crucial for further purifying the SBR effluent and mitigating the membrane fouling load.

The influence of different nanoparticle adsorbents on the pollutant removal efficiency

The comparative results of different nanoparticle adsorbents on the removal efficiency of various pollutants demonstrated significant differences in COD removal effects among various adsorbents with removal rates generally increasing as the addition concentration rises. γ-Fe_2O_3 performed the best, achieving a COD removal rate of 75.51% at 2.0 g/L, remarkably superior to Fe_3O_4 and α-Fe_2O_3. GAC showed the weakest effect at only 58.65%. γ-Fe_2O_3 outperformed other adsorbents at all concentration levels, exhibiting stronger adsorption activity and affinity for organic pollutants, making it suitable as a functional material for efficiently removing COD from industrial wastewater (Figure 1a). All adsorbents demonstrated high efficiency in the removal of TP with iron-based nanoparticles exhibiting particularly outstanding performance. γ-Fe_2O_3 achieved a removal rate of 97.66% at a concentration of 2.0 g/L, leading Fe_3O_4 and α-Fe_2O_3, and far exceeding GAC's 75.77%. γ-Fe_2O_3 maintained consistently high removal performance at all addition concentrations, indicating its strong complexation and precipitation capabilities for phosphate ions with stable and superior adsorption performance. In contrast, GAC showed slow growth in removal

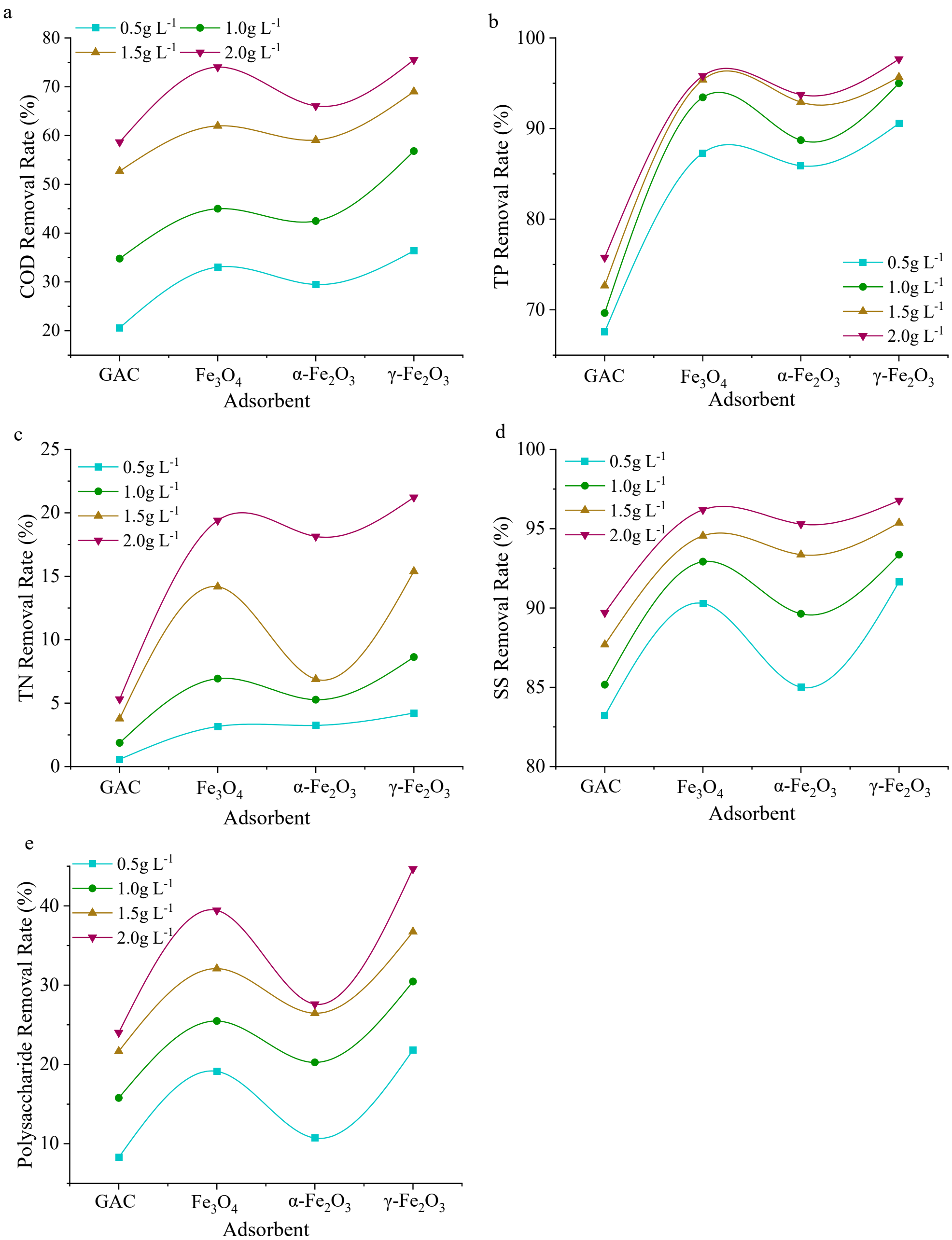

Figure 1. Comparison of the removal efficiency of various pollutants by different nanoparticle adsorbents. **a.** COD. **b.** TP. **c.** TN. **d.** SS. **e.** Polysaccharides.

rate with limited TP adsorption capacity, making it difficult to meet the purification requirements of high-intensity industrial wastewater (Figure 1b). The overall performance of each adsorbent in TN removal was relatively limited, still significantly constrained by its physical adsorption mechanism. γ-Fe_2O_3 exhibited the best performance at 2.0 g/L with a removal rate of 21.22%, higher than Fe_3O_4 and α-Fe_2O_3, while GAC had almost no removal capacity at only 5.31%. The surface functional groups and charge characteristics of nanoparticles promoted the adsorption of nitrogen species to a certain extent, particularly the enhanced denitrification efficiency of γ-Fe_2O_3 at higher concentrations, which revealed its potential application value in strengthening nitrogen removal (Figure 1c). The removal of SS imposed higher requirements on particle adsorption capacity. γ-Fe_2O_3 ranked first with a removal rate of 96.78% at a concentration of 2.0 g/L followed by Fe_3O_4 and α-Fe_2O_3 at 96.19% and 95.29%, respectively. GAC was relatively inferior at 89.70% (Figure 1d). Due to their high specific surface area and good dispersibility, iron-based nano-oxides could more fully capture fine particles, which demonstrated substantial scavenging potential for SS and enhanced their engineering adaptability in membrane fouling pretreatment. γ-Fe_2O_3 still exhibited excellent performance in scavenging polysaccharides in EPS, achieving a removal rate of 44.66% under 2.0 g/L conditions, which was markedly better than 39.43% for Fe_3O_4 and 27.60% for α-Fe_2O_3, while GAC was only 24.01% at the same concentration (Figure 1e). Nanoscale γ-Fe_2O_3 exhibited high surface reactivity that significantly disrupted the sugar chain network in EPS structures. This enhanced disruption improved flocculation and binding effects, establishing γ-Fe_2O_3 as the most promising adsorbent for membrane fouling control. Its advantages were particularly remarkable in controlling extracellular polymer-related pollution. A comprehensive analysis of the removal effects of various pollution factors showed that the three iron-based nano-oxide adsorbents all outperformed traditional GAC. Moreover, their pollutant scavenging capacity increased with concentration, exhibiting a good dose-response relationship. Among them, γ-Fe_2O_3 maintained the highest removal rate in all indices, especially showing obvious advantages in scavenging key pollutants such as COD, TP, and polysaccharides, highlighting its excellent surface activity and adsorption selectivity. Fe_3O_4 and α-Fe_2O_3 both demonstrated stable purification potential. In contrast, GAC had limited treatment capacity, especially in controlling complex components such as nitrogen and extracellular polymers. Overall, γ-Fe2O3 had a stronger broad-spectrum adsorption capacity and was a functional material worthy of priority consideration in the pretreatment of high-intensity industrial wastewater.

Characterization and analysis of nanoparticles

The surface charge characteristics and particle size distribution of adsorbents notably influenced their stability in water, flocculation capacity, and pollutant capture efficiency. Particularly in composite pretreatment-membrane filtration coupling systems, interfacial behaviors directly affected adsorption-separation efficiency. The comparative results of zeta potential and average particle size for four adsorbents of GAC, nano-Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3 demonstrated distinct differences in surface electrical properties and particle size characteristics among the four adsorbents, which remarkably influenced their adsorption and dispersion performance. γ-Fe_2O_3 showed the lowest zeta potential of -11.45 mV and the largest particle size of 684.4 nm, characteristics that promoted particle agglomeration and flocculation. Fe_3O_4 and α-Fe_2O_3 exhibited intermediate properties with zeta potentials of -12.23 mV and -14.9 mV, respectively, along with moderate particle sizes, resulting in stronger interfacial activity. GAC showed the lowest electrical potential and smaller particle size, displaying inferior stability and adsorption capacity compared to iron-based nano-oxides (Figure 2). The results of comprehensive analysis indicated that iron-based nanoparticles possessed superior fundamental adsorption characteristics.

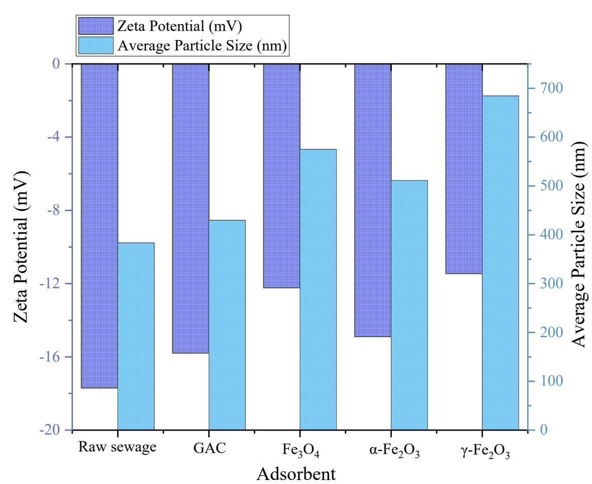

Figure 2. Average particle size and zeta potential of different adsorbents.

Analysis of membrane flux variation

To evaluate the effectiveness of different nanoparticle adsorbents in mitigating membrane fouling, the decay process of membrane performance was tracked by analyzing the trend of normalized membrane flux ratio (J/J_0) over operation time. The J/J_0 data for Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3 at various dosing concentrations when the filtration volume was 200 mL demonstrated that γ-Fe_2O_3 performed the best at 2.0 g/L with a flux maintenance rate as high as 0.658, far exceeding GAC and raw wastewater, which indicated its significant advantage in inhibiting the formation of fouling layers on the membrane surface. Fe_3O_4 showed its J/J_0 of 0.588, while α-Fe_2O_3 showed 0.497, both reflecting the fouling mitigation effect of increased concentrations. GAC had a moderate overall performance, lower than the other three nanomaterials, which indicated that GAC's particle size, charge properties, or interfacial behaviors were less effective in membrane fouling control compared to iron oxide particles (Figure 3). The clear performance differences among adsorbents suggested that nano-structure characteristics might be a key factor.

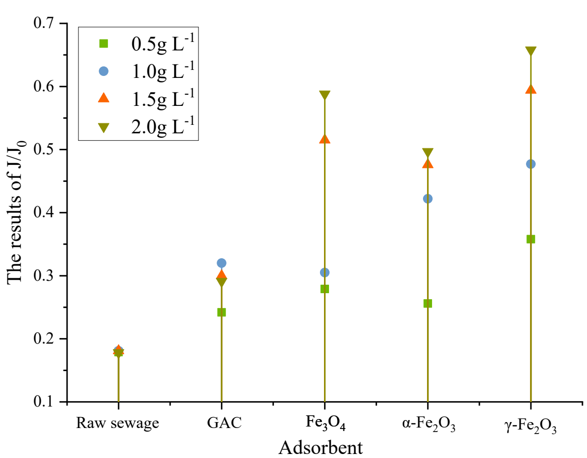

Figure 3. *J/J_0* results of diverse nanoparticle adsorbents.

Pollution mechanism and correlation analysis based on the XDLVO theory

The XDLVO theory is a theoretical framework used to describe the interactions between colloids, particles, or pollutants and the membrane surface. Based on the classic DLVO theory, it incorporates acid-base interactions into consideration. Concurrently, it comprehensively analyzes the contributions of Lifshitz–van der Waals potential (ULW), acid-base potential (UAB), and electrostatic potential (UEL) to the total interaction energy (U_{total}), which enables more accurate evaluation of the energy barrier for the adsorption or repulsion behavior of pollutants on the membrane surface. The results showed that there was a specific separation distance between the membrane and pollutants, at which the repulsive force reached its maximum value (i.e., the energy barrier). This energy barrier reflected the minimum energy required for pollutants to adsorb onto the membrane surface. Based on this, the pollutant-membrane interaction energy under the condition of sub-minimum energy was calculated for various adsorbent treatments, and the results showed that different adsorbent treatments substantially affected the interaction energy between pollutants and the membrane surface. Before raw water treatment, the total interaction energy was 38.6 kT, among which the electrostatic potential (UEL) was 72.5 kT, serving as the main repulsive force. After GAC treatment, the total interaction energy increased to 58.1 kT, and the UEL increased to 100.3 kT, indicating a certain alleviating effect on membrane fouling. Iron-based nanoparticles further increased the total interaction energy to 89.8 kT for Fe_3O_4, 93.1 kT for α-Fe_2O_3, and the highest value of 125.2 kT for γ-Fe_2O_3. Their electrostatic potential was 155.6 kT, 160.5 kT, and 208.1 kT, respectively (Figure 4). The nanoparticles, especially γ-Fe_2O_3, significantly enhanced the repulsive force between the membrane and pollutants, increasing the energy required for pollutants to overcome the energy barrier, which effectively inhibited the adsorption of pollutants on the membrane surface and the formation of membrane fouling. Although the Lifshitz–van der Waals potential and acid-base potential were negative, their absolute values increased with the type of nanoparticles, which indicated that nanoparticles played a synergistic role in improving the surface interface interaction. In general, the γ-Fe_2O_3 adsorption pretreatment could maximize the membrane's anti-fouling ability.

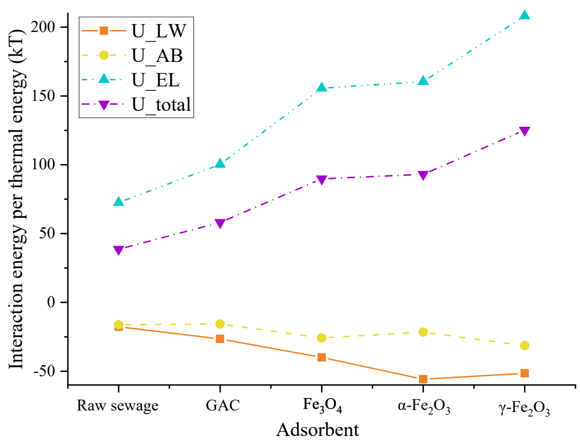

Figure 4. Comparison of pollutant-membrane interaction energy of different nanoparticle adsorbents.

Discussion

This study confirmed that iron-based nano-oxides, as adsorption pretreatment materials, could significantly enhance the anti-fouling performance of the AGMBR system. Namdeti *et al*. emphasized the necessity of deeply integrating biological processes with membrane technology [20]. By introducing an upstream adsorption unit, this study effectively reduced the residual pollutant load after biological treatment, thereby optimizing the operational efficiency of this integrated system. The experimental results demonstrated that γ-Fe_2O_3 exhibited the best broad-spectrum adsorption performance at a dosage of 2.0 g/L, achieving removal rates of 75.51% for COD and 97.66% for TP, significantly outperforming traditional GAC. This excellent performance was attributed to the abundant active sites provided by the high specific surface area of the nanomaterial, enabling the efficient removal of dissolved organic matter and extracellular polymeric substances through the synergistic effects of surface complexation and physical interception, which created more favorable water quality conditions for subsequent membrane separation. In-depth mechanistic analysis indicated that the interfacial properties of nanoparticles played a decisive role in mitigating membrane fouling. Sharma *et al*. discussed the latest trends in utilizing smart nanomaterials for wastewater treatment [21], pointing out that the microstructure of materials directly affected the efficiency of its interaction with pollutants. The calculated results based on XDLVO theory in this study were consistent with this view that, after treatment with γ-Fe_2O_3, the total interaction energy between pollutants and the membrane surface significantly increased from 38.6 kT in the raw water to 125.2 kT. The enhancement of the electrostatic repulsion barrier reaching 208.1 kT effectively increased the difficulty for pollutants to overcome the energy barrier and adsorb onto the membrane surface. Furthermore, correlation analysis confirmed that the Zeta potential and particle size of the mixed liquor were significantly negatively correlated with membrane resistance, which implied that γ-Fe_2O_3 increased particle stability through charge neutralization and promoted the agglomeration of fine particles *via* bridging effects, forming a loosely structured filter cake layer with good permeability. Consequently, the membrane flux retention rate was maintained at a relatively high level of 0.658, significantly outperforming the control group without adsorbent addition. Although iron-based nanomaterials exhibited excellent performance under laboratory conditions, their sustainability and technical limitations must be comprehensively considered when transitioning toward practical engineering applications. Saleh systematically investigated nanocomposites for removing hazardous pollutants and their implications for water recycling sustainability [22]. Drawing on this perspective, the present study found that, while γ-Fe_2O_3 was highly effective in removing organic matter and phosphorus, its removal efficiency for TN relied primarily on physical adsorption, yielding relatively limited efficiency. Furthermore, the dead-end filtration mode employed in this experiment differed from industrial cross-flow filtration systems. Therefore, future research should focus on surface functionalization of nanomaterials to construct multi-component synergistic adsorbents, enhancing selective removal capabilities for complex nitrogen species and conducting long-term operational experiments under continuous-flow cross-filtration conditions to evaluate the stability and recovery-regeneration potential of nano-adsorbents, thereby advancing the engineering application of this technology in advanced treatment of high-strength industrial wastewater.

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