**ABSTRACT**

A novel sinusoidal alternating current coagulation (SACC) technique was used to remove the Zn$^{2+}$ from wastewater in the present study. The response surface methodology was used to analyze the effect of current density, time, initial pH and initial Zn$^{2+}$ concentration in order to obtain the optimum removal efficiency and to lower energy consumption. The results show that SACC with a current density of 0.31 A·m$^{-2}$ applied to treat wastewater containing 120 mg·dm$^{-3}$ Zn$^{2+}$ at pH $= 9$ for 21.3 min can achieve a removal efficiency of Zn$^{2+}$ of 98.80%, and the energy consumption is 1.147 kWh·m$^{-3}$. The main component of flocs produced in SACC process is Fe$_5$O$_7$OH·4H$_2$O (HFO). Large specific surface area and good adsorption performance of HFO are demonstrated. There is strong interaction between Zn$^{2+}$ and HFO. Zn$^{2+}$ is adsorbed and trapped by HFO and then co-precipitated. Freundlich adsorption isotherm model and pseudo-second order kinetics model explained the Zn$^{2+}$ adsorption behavior well. The Zn$^{2+}$ adsorption on HFO is an endothermic and spontaneous process.

**HIGHLIGHTS**

- Zn$^{2+}$ in wastewater was successfully removed by a sinusoidal alternating current coagulation (SACC) process.
- The optimum process was obtained by adopting response surface methodology.
- The mechanism of Zn$^{2+}$ removal by SACC process is explained.
- A detailed mechanism analysis of Zn$^{2+}$ adsorption behavior was conducted.

**INTRODUCTION**

Many industrial wastewaters from electroplating, steel industry and mining have had a major impact on the environment (Smedley & Kinniburgh 2002). Many kinds of heavy metals such as copper, nickel, chromium, silver and zinc in wastewater will cause great harm to the environment if they are discharged directly (Azimi et al. 2017). These toxic heavy metal ions are easily enriched in the living organisms through the food chain. After accumulation and migration, they pose a series of serious hazards to ecosystems and human health (Song et al. 2017). For example, excessive Zn$^{2+}$ can seriously damage the immune function of the human body and cause harm to human health. Therefore, industrial wastewater should be treated before discharge to meet the discharge standard.

Numerous treatment techniques have been adopted to remove Zn$^{2+}$ in the wastewater. These include precipitation, adsorption, ion exchange, ultra-filtration, reverse osmosis and oxidation/filtration (Ozaki et al. 2002; Esmi et al. 2014; Ganiyu et al. 2015; Qian & Li 2015; Víctor-Ortega et al. 2016a, 2016b). Among the various techniques, the chemical coagulation method is widely used for the treatment of
heavy metals in industrial wastewater because of its simplicity and high efficiency (Zhu et al. 2005). However, this treatment method requires higher cost and will also cause secondary pollution to our environment. The shortcomings have encouraged many researchers to seek other new treatments to remove heavy metals from industrial wastewater (Emamjomeh & Muttucumaru 2009).

Compared with the traditional chemical coagulation treatment, the electrocoagulation (EC) technology has the advantages of simple operation, no secondary pollution, high removal efficiency, relatively low cost and easy automation. Chen et al. (2018) focused on the Zn$^{2+}$ removal from a synthetic wastewater by EC with aluminum electrodes. It indicated that Zn$^{2+}$ removal efficiency increased with the increase of current density and residence time. Almost all Zn$^{2+}$ (50 mg·dm$^{-3}$) was removed in 20 minutes EC treatment with energy consumption of 0.35 kWh·m$^{-3}$. Brahmi et al. (2015) studied the removal of zinc ions from synthetic and industrial Tunisian wastewater by EC using aluminum electrodes. Optimum conditions for zinc removal were found to be pH value of 7, a current density of 7.35 mA·cm$^{-2}$, an inter-electrode potential of 5 V, a conductivity of 5.3 mS·cm$^{-1}$, and an EC time of 30 min; the removal efficiency of Zn$^{2+}$ could reach 98.96%. EC as an electrochemical technique has been successfully applied to remove heavy metals from various types of industrial wastewater, but more research should focus on reducing electrode loss and power consumption. In particular, the formation of an oxide passivation layer on the electrode surface hinders continuous dissolution of iron and electron transfer. As a result, the removal efficiency of heavy metal will be reduced and energy consumption will be increased.

The application of alternating current coagulation (ACC) can effectively overcome these shortcomings. Furthermore, the operating cost is lower than that of the direct current coagulation (DCC). Vasudevan & Lakshmi (2011) studied the removal of cadmium from water by ACC and DCC using aluminum alloys as dissolved electrodes. At a current density of 0.2 A·dm$^{-2}$ and in pH 7.0 solution, the energy consumption of ACC and DCC was 0.454 and 1.002 kWh·m$^{-3}$ and the removal efficiencies were 97.5% and 96.2%, respectively.

In our previous research, sinusoidal alternating current coagulation (SACC) technique has been proved to be an efficient method to remove heavy metals in wastewater (Xu et al. 2019). The output waveform of sinusoidal alternating current is a sinusoidal function. The prepared nanoferrum collosol by SACC technique has a smaller size and a larger specific surface area than that produced by DCC, thus resulting in a great advantage in the aspects of heavy metal ion removal efficiency and low sludge yield. Up to now, there are few researches on the electrochemical treatment of wastewater by SACC technique at home and abroad, and a systematic and comprehensive analysis and demonstration are lacking (Xu et al. 2020).

The process of Zn$^{2+}$ removal from the aqueous phase by adsorbents can be described by kinetic models. Adsorption kinetics are explained by mass transfer, diffusion control, chemical reaction and particle diffusion (Barhoumi et al. 2017). The adsorption isotherm model is used to predict the capacity of the EC adsorbents. In order to understand the EC dynamic mechanism, pseudo-first order kinetic, pseudo-second order kinetic and intra-particle diffusion models were fitted with the experimental data (Xu et al. 2011). The Freundlich isotherm of adsorption, the Langmuir isotherm, the Dubinin–Radushkevich (D–R) isotherm and the Temkin adsorption equation were used to describe the adsorption behavior in the EC process. Temperature plays an important role in the adsorption of metal ions. The solution temperature also affects the adsorption capacity. Activation Gibbs free energy ($\Delta G^*$), activation enthalpy ($\Delta H^*$) and activation entropy ($\Delta S^*$) are the important thermodynamic parameters sensitive to temperature.

As mentioned above, although the existing DCC process is certainly effective for treatment of various industrial wastewaters, there are still obvious deficiencies in reducing electrode passivation and energy consumption. There are few reports about the treatment of Zn$^{2+}$ by ACC process. In this paper, the effects of initial pH (pH$_0$), current density ($j$), initial concentration ($c_0$) and electrolysis time ($t$) on the removal rate of Zn$^{2+}$ were studied by using SACC technology. The optimization of various process parameters was analyzed with response surface methodology (RSM) in order to improve Zn$^{2+}$ removal efficiency and reduce processing costs. The mechanism of Zn$^{2+}$ removal by SACC was studied by means of scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

**MATERIALS AND METHODS**

**Chemicals and reagents**

All general reagents and solvents are commercially available and used without further purification. The iron piece was supplied by Aerospace Kaitian Technology Co., Ltd (volume...
25 × 25 × 2 mm³). Zinc sulfate heptahydrate (ZnSO₄·7H₂O), sodium chloride (NaCl), ferric chloride (FeCl₃), ethanol (CH₃CH₂OH), zinc reagent (C₂₀H₁₅N₄NaO₆S), sulfuric acid (H₂SO₄), ammonia (NH₃·H₂O), etc., as analytical grade, were purchased from Changsha Pengjin reagent distributor and Sinopharm Group. Self-made ultrapure water (18 MΩ·cm⁻¹) was used in the experiment.

**Experimental device and operation**

The 10 dm³ electrolytic cell was made of polymethyl methacrylate. Ten titanium baskets (the iron fragments in the titanium basket) were used as five groups of parallel sacrificial anode and cathode. The electrode distance between each titanium electrode was 10 mm. The SAC power source (CHP-500, 45–400 Hz and 0–300 V) provided electrical energy during electrolysis. The schematic diagram of the SACC system is shown in Figure 1. All experiments were carried out at room temperature of 25 ± 0.5 °C.

**RSM experimental design**

The Box–Benhnken design (BBD) method was used to design four factors (pH₀, t, c₀) that have a great influence on the single factor experiment in order to obtain the experimental conditions required for the optimum treatment of Zn²⁺ wastewater. The individual variables (x₁, x₂…xₖ) and the response (y) can be related as follows (Saravanaathamizhan et al. 2007):

\[
y = f(x₁, x₂, \ldots, xₖ) + \varepsilon
\]

(1)

In this study, Design-Expert 8.0.6 (Stat-Ease Inc., USA) software was used to design the experiment. The second order model fitting equation for Zn²⁺ removal efficiency is as follows:

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon
\]

(2)

where Y: response value; β₀: offset term offset coefficient; βᵢ: linear offset coefficient; βᵢᵢ: second order offset coefficient; βᵢⱼ: interaction coefficient; xᵢ and xⱼ are the independent variables.

**Analysis method**

**Determination of Zn²⁺ concentration and expression of removal rates**

The concentration of Zn²⁺ in the solution was measured using an ultraviolet spectrophotometer (Ople UV1800, Shanghai) (Gumus et al. 2005; Vieira et al. 2008; Uddin et al. 2013; Zhou et al. 2019). A Zn²⁺ standard solution with pH 9 was prepared and zinc reagent was added to develop color for 10 min; the absorbance at 620 nm was measured with a UV-vis spectrophotometer. The regression equation is \(Y = 0.341X + 0.003\) (X: Zn²⁺ concentration, Y: absorbance). The linear correlation coefficient (R²) of the fitting curve is 0.9986. The removal rate (η) of Zn²⁺ can be calculated by following equation:

\[
\eta = \frac{c_0 - c}{c_0} \times 100\%
\]

(3)

where c₀ is the initial concentration (mg·dm⁻³) and c is the concentration (mg·dm⁻³) at t (min) after EC process.

**Characterization of the coagulations**

The surface morphology and elemental content of the flocs were characterized by using SEM (Hitachi S-4800, Japan) with an energy-dispersive X-ray spectroscopy (EDS) analyzer. FT-IR spectra were obtained by using a MAGNA-IR 560 spectrometer (Nicolet, USA) with the KBr tablet method at room temperature. To investigate the crystalline structure, the XRD patterns were obtained by using an X-ray diffractometer (Shimadzu 6100, Japan) with Cu Kα radiation (λ = 1.5418 Å). The XPS measurements were carried out by using a Physical Electronics PHI 5000 Versa Probe spectrometer (USA) with a monochromatic Al Kα source operated at 300 W.
Adsorption process fitting methods

Analysis of adsorption kinetics

The process of Zn$^{2+}$ caught by adsorbents from the wastewater can be fitted by kinetic models. The adsorption efficiency and the feasibility of large-scale application of the adsorption material are clearly understood. The pseudo-first order kinetic model equation is as follows (Chungsying et al. 2006):

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

(4)

where $q_e$ (mg·g$^{-1}$) is the adsorption amount of the adsorbent when the solution reaches the adsorption equilibrium, $q_t$ (mg·g$^{-1}$) is the adsorption amount of the adsorbent at a certain moment, and $k_1$ (min$^{-1}$) is the rate constant of the first order adsorption.

The second order kinetic equation is as follows (Montillo et al. 2008):

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

(5)

where $k_2$ (g·mg$^{-1}$·min$^{-1}$) is the rate constant of a pseudo-second order dynamic adsorption.

The pseudo-first order kinetics and the pseudo-second order kinetics cannot explain the intra-diffusion mechanism in the adsorption process, but the intra-particle diffusion model can well describe the different rate stages of the adsorption internal diffusion. The internal diffusion model is as follows (Waranusantigul et al. 2003):

$$q_t = k_{id} t^{1/2} + I$$

(6)

where $k_{id}$ (mg·g$^{-1}$·min$^{1/2}$) is the internal diffusion rate constant of different stages, $i$ is the different stage, $I$ corresponds to the boundary layer thickness.

Isotherm models

Langmuir isotherm equation. The linearized Langmuir adsorption isotherm model is expressed as (Langmuir 1916; Abdelwahab 2008):

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m}$$

(7)

where $q_e$ is the adsorption amount at the equilibrium concentration $c_e$, $q_m$ is the maximum single layer adsorption amount, and $b$ is the Langmuir constant associated with the adsorption energy.

Freundlich isotherm equation. The mathematical expression of the Freundlich model can be written as (Chen et al. 2009):

$$\lg q_e = \lg K_f + n \lg c_e$$

(8)

where $K_f$ is the Freundlich constant, which is related to the adsorption capacity; $n$ is the energy or intensity of adsorption; $c_e$ (mg·dm$^{-3}$) is the equilibrium concentration of Zn$^{2+}$ adsorption.

Dubinin–Radushkevich isotherm model equation. Dubinin and Radushkevich proposed another isothermal model that can be used to analyze equilibrium data. It does not assume a uniform surface or constant adsorption potential energy, but rather is used to estimate the average Gibbs function ($G$) of adsorption. This model equation is as follows (Lashaki et al. 2012):

$$\ln q_e = \ln q_e^0 - 2BRT \ln \left(1 + \frac{1}{c_e} \right)$$

(9)

where $B$ is the constant related to the molar adsorption Gibbs function, and $q_e$ is the D–R isotherm constant, which is related to the adsorption degree of the adsorbate on the surface of adsorbent. The constant $B$ gives the average Gibbs function $G$ adsorbed by the adsorbate as it moves from infinity to the solid surface in solution, and gives the relationship between them:

$$G = \frac{1}{\sqrt{2B}}$$

(10)

Temkin adsorption. The Temkin adsorption isotherm model assumes that the heat of adsorption decreases linearly rather than logarithmically. The linearized form of the Temkin isotherm is given as follows (Aysu & Kıcıl 2015):

$$q_e = B \ln (A_t) + B \ln (c_e)$$

(11)

where $A_t$ is the Temkin isotherm equilibrium binding constant (dm·g$^{-1}$) and $B$ is the constant related to heat of sorption (J·mol$^{-1}$).

Adsorption thermodynamics

The thermodynamic parameters of the change of adsorption Gibbs free energy $\Delta G^\circ$, the change of adsorption enthalpy
and the change of adsorption entropy \( \Delta S^r \) were found by temperature experiment of the adsorption process. The relevant \( \Delta H^r \) and \( \Delta S^r \) can be calculated using the following equation:

\[
\ln K_d = \frac{\Delta S^r}{R} - \frac{\Delta H^r}{RT}
\]

(12)

where \( K_d \) is the distribution coefficient. \( \Delta G^r \) and \( K_d \) are calculated by the following equation:

\[
\Delta G^r = -RT \ln K_d
\]

(13)

\[
K_d = \frac{q_e}{c_e}
\]

(14)

where \( q_e \) (mg·g⁻¹) and \( c_e \) (mg·dm⁻³) are the adsorption amount of Zn²⁺ in the solution adsorbed by the ferric oxide hydrate (HFO) adsorbent and the equilibrium concentration of Zn²⁺ in the solution, respectively, when equilibrium is reached.

RESULTS AND DISCUSSION

**BBD experimental design**

The experimental design of BBD is shown in Table 1. \( X_1, X_2, X_3 \) and \( X_4 \) in the table represent the four factors, namely reaction time (min), initial pH, initial concentration (mg·dm⁻³), and current density (A·cm⁻²).

BBD and experimental data are shown in Table S1 (Supplementary Material). The response surface optimization experimental data analysis is shown in Table 2. Analysis of variance results imply that both the models were significant because the model F-values obtained were 2.31 and 20.33 respectively and the corresponding \( p \)-values were <0.0001 for both the models. The above data indicate that the RSM model can be used to predict experimental results (Kobya et al. 2010). The fitting quadratic model can well explain the influence of various factors on the Zn²⁺ removal by SACC process.

**Table 1 | Range of different factors investigated by the BBD design**

<table>
<thead>
<tr>
<th>Coding</th>
<th>Factor (unit)</th>
<th>1</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_1 )</td>
<td>Reaction time (min)</td>
<td>5</td>
<td>17.5</td>
<td>30</td>
</tr>
<tr>
<td>( X_2 )</td>
<td>Initial pH</td>
<td>4</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>( X_3 )</td>
<td>Initial concentration (mg·dm⁻³)</td>
<td>10</td>
<td>65</td>
<td>120</td>
</tr>
<tr>
<td>( X_4 )</td>
<td>Current density (A·cm⁻²)</td>
<td>0.04</td>
<td>0.62</td>
<td>1.2</td>
</tr>
</tbody>
</table>

By calculation of BBD design on four factors, a quadratic regression model of Zn²⁺ removal efficiency \( Y_1(\text{Re}) \) and energy consumption \( Y_2(\text{ENC}) \) as response values is obtained through SACC process, as shown in the formula below.

\[
Y_1(\text{Re}) = 60.28438 + 1.77012 X_1 + 0.21282 X_2 - 0.20971 X_3 + 26.45590 X_4 - 0.095 X_1 X_2 + 4.66909 \times 10^{-3} X_1 X_3 - 0.9869 X_1 X_4 + 0.026848 X_2 X_3 - 1.22701 X_2 X_4 + 0.024295 X_3 X_4
\]

\[
Y_2(\text{ENC}) = -2.07993 + 0.086079 X_1 + 0.030931 X_2 - 4.88335 \times 10^{-3} X_3 + 3.46749 X_4
\]

A Pareto chart is often used to determine the significance of each factor term for response values. The length of each bar in Figure 2 represents its effect on the response value. The lowest reference value of

![Figure 2 | Pareto chart for the standardization of effect on removal efficiency (The dotted line is 95% confidence; to the right side of the dotted line, the factor sub-term is a more significant term).](http://iwaponline.com/wst/article-pdf/82/9/1950/781326/wst082091950.pdf)
standardization impact is $P = 0.05$, see the vertical dotted line in Figure 2. When the value of standardization impact of a factor exceeds 0.05 (dashed line position), i.e., on the right side, it indicates that there is statistical significance of the factor sub-term.

From Figure 2, the impact lengths of all factor terms of $X_4$, $X_1$, $X_2X_4$, $X_1X_4$, $X_2$, $X_3$, and $X_1X_2$ exceed the reference dotted line, indicating that their responses are more significant. The more significant response intensity order from strong to weak is current density, electrolysis time, interaction of initial pH and current density, and interaction of current density and electrolysis time. The SAC density has the most significant effect on the Zn$^{2+}$ removal in SACC process. The interaction of current density and initial pH, and current density and electrolysis time have very significant effects. Other terms have less significant effect.

Figure S1 (Supplementary Material) clearly reflects the effect of the interaction between current density and initial pH and the interaction between current density and time on Zn$^{2+}$ removal efficiency. The other two interaction factor sub-terms are close to the reference dotted line. Iron electrode is dissolved in the solution to produce a large amount of Fe$^{2+}$ through SAC electrolysis and further oxidized into Fe$^{3+}$ by O$_2$, and then forms a series of complex hydroxy polynuclear complexes and hydroxides in solution (Xu et al. 2017). These nano-hydroxy materials, due to their large surface area and thus their strong adsorption characteristic, become excellent flocculants for the removal of contaminants (Xu et al. 2019). However, improper pH is not conducive to the removal of Zn$^{2+}$ by SACC. The optimal pH should be controlled at 9.

Process parameters (pH, current density, initial Zn$^{2+}$ concentration and electrolysis time) were optimized using the calculation of Design-Expert 8.0.6 software. All variables were kept within the corresponding range, and the target value of the Zn$^{2+}$ removal efficiency was set to 100%. The optimum process values for the removal efficiency calculated by the software are $c_0 = 120$ mg·dm$^{-3}$, pH = 9, $j = 0.31$ A·m$^{-2}$, $t = 21.3$ min. The correctness of calculated values was verified by performing three parallel experiments under the optimal process conditions obtained from software optimization. Under the optimal process conditions, the Zn$^{2+}$ removal efficiency by SACC process reached 98.80%, and the energy consumption was 1.147 kWh·m$^{-3}$. The results show that the experimental value of the Zn$^{2+}$ removal efficiency is very close to the theoretical value. The RSM method is correct for application in analysis of the SACC process of Zn$^{2+}$ removal in wastewater.

**Floc characterization**

**SEM characterization and EDS analysis**

Under the same conditions ($c_0 = 120$ mg·dm$^{-3}$, pH = 9, $j = 0.31$ A·m$^{-2}$, $t = 21.3$ min), the iron sol was prepared by DCC and SACC respectively, and its surface state was observed by SEM. The surface topography of the precipitate is shown in Figure 3. It is obvious that the flocs exhibit different morphological features. Some coarse blocky fragments were observed in the flocculation produced by DCC, as shown in Figure 3(a1). The flocculation produced by SACC appears as a flocculent nanosphere with a larger specific surface area, which is more conducive to the adsorption of heavy metals in wastewater, as shown in Figure 3(a2).

As shown in Figure 3(b1) and 3(b2), the EDS patterns of flocculants produced by DCC and SACC methods demonstrate that the main elements in the HFO are C, O, Fe and Zn. The mass fractions of Zn are 2.93% for DCC and 15.87% for SACC, respectively. This indicates that the ferric hydroxide produced by SACC process is more efficient for the Zn$^{2+}$ removal from wastewater than that by DCC because of the adsorption performance of nanospheres with high specific surface area produced by SACC process (Xu et al. 2019).

**FTIR and XRD analysis of flocculants**

Figure 4(a) shows the corresponding XRD pattern of the dried precipitate produced by SACC treatment in 100 mg·dm$^{-3}$ Zn$^{2+}$ solution for 30 min. It can be seen from the XRD spectrum that the precipitate formed by applying a SAC electrolytic iron electrode in the solution has only one diffraction peak, corresponding to the (110) crystal face of ferric hydroxide hydrate (HFO) (Fe$_5$O$_7$OH·4H$_2$O JCPDS: 29-0712) at 2θ = 56.649°. Because the crystallization of ferric hydroxide is a very slow process, most ferric hydroxide is amorphous or has low crystallinity. In the XRD spectra of the precipitate produced from Zn$^{2+}$ solution by SACC treatment for 30 min, the diffraction peaks of 2θ = 27.334° and 53.044° are corresponding to (110) and (212) crystal planes of Zn(OH)$_2$ (JCPDS: 20-1437), and the diffraction peaks of 2θ = 60.479° are corresponding to (111) crystal plane of Zn(OH)$_2$ (JCPDS: 38-0385). The diffraction peak at 2θ = 53.110° corresponds to the (422) crystal plane of ZnFe$_2$O$_4$ (JCPDS: 22-1012). The (110) crystal plane of ferric hydroxide hydrate (HFO) (Fe$_5$O$_7$OH·4H$_2$O JCPDS: 29-0712) corresponds to 2θ = 56.649°. Therefore, it is found that HFO can easily adsorb Zn$^{2+}$ in wastewater.
through comparison of the main diffraction peak on the XRD standard card.

Figure 4(b) shows the infrared spectrum of the HFO-Zn\(^{2+}\) with a wavenumber of 3,443 cm\(^{-1}\) as the stretching vibration peak of -OH; the absorption peak with a wavenumber of 1,609 cm\(^{-1}\) is the H-O-H bending vibration peak (Balasubramaniam & Ramesh Kumar 2006; Goldberg & Johnston 2001). The strong peak at 3,113.1 cm\(^{-1}\) is due to the O-H stretching vibration in the Fe(OH)\(_3\) structure. The peak of 1,076 cm\(^{-1}\) and the peak of 480 cm\(^{-1}\) correspond to the tensile vibrations of Fe-O (Fe\(_2\)O\(_3\), Fe\(_{3-x}\)O\(_4\)) and Zn-O, respectively. The main diffraction peaks are zinc-iron compounds (ZnFe\(_2\)O\(_4\), PDF: 22-1012) and ferric hydroxide hydrate (HFO) (Fe\(_2\)O\(_3\)·OH·H\(_2\)O PDF: 29-0712), which are consistent with the conclusions described by the previous XRD spectra.
XPS analysis of flocculants

Figure 5 shows the XPS spectrum of a precipitate produced by SACC. The main elements are C, O, Zn and Fe (Figure 5(a)). The two peaks at 1,022.6 eV and 1,045.6 eV correspond to Zn2P (Figure 5(c)) of the XPS spectrum of Zn2+ 2P3/2 and Zn2+ 2P1/2. Iron signal appears at 711.91 eV (Figure 5(b)), which is typically the peak iron hydroxide.

As shown in the EDS spectrum (Figure 3(b2)), the Zn peaks in the flocs are significant and the Zn mass composition reaches 15.87 wt%. XRD analysis also indicates that there are deposits of Zn(OH)2 and ZnFe2O4 compounds (Figure 4(a)). XPS spectra further confirm that the clear characteristic peak of Zn2+ at 1,019.8 eV exists (Figure 5(c)), which indicates that the precipitate is mainly composed of HFO and co-precipitated Zn2+. Zn2+ is adsorbed by HFO and then co-precipitated. In summary, it can be concluded that Zn2+ removal by SACC is attributed to the combined effects of three steps: (a) formation and assembly of hydroxides to produce ferrum collosol through electrolysis of Fe electrodes, especially under weak acidic or alkaline medium; (b) adsorption of ferric hydroxide flocculants (ferrum collosol); (c) deposition of iron sol containing Zn.

Hydrogen bubbles generated during the electrocoagulation will play a role of electric flotation and will bring the suspension of assembled colloidal particles to the surface of the water. In this way, the separation process between flocculation and solution can be effectively accelerated.

Analysis of adsorption mechanism

Table S2 lists the calculation results of the kinetic parameters of pseudo-first order, pseudo-second order and intra-particle diffusion models for SACC. The adsorption of Zn2+ by SACC obviously obeys the pseudo-second order kinetic equation. From Figure 6(c), the curve of qt versus \( t^{1/2} \) can be divided into two linearity ranges with time, which indicates that the Zn2+ diffusion in HFO has two internal diffusion modes. The first line segment is the initial diffusion phase. The diffusion of adsorbed Zn2+ occurs on the outer surface of the HFO. The diffusion rate \( k_{1d} \) is significantly larger than \( k_{2d} \). The rate of the first phase is very fast. When the Zn2+ adsorption on the outer surface of the HFO reaches saturation, Zn2+ enters the interior of the HFO through the internal micropores of the
HFO. As the adsorption amount continues to increase, the internal diffusion resistance on the surface of the internal particles increases. Afterwards, the internal diffusion rate gradually slows down and trends to stabilization.

The SACC technique was used to produce the fresh highly active adsorbent of HFO in wastewater. The wastewater with 20 mg·dm$^{-3}$ Zn$^{2+}$ was treated by SACC for 30 min at room temperature. Figure 7(a) and 7(b) show the Langmuir curve of Zn$^{2+}$ adsorption and Freundlich curve of Zn$^{2+}$ adsorption. We omitted the figures of D-R and Temkin curves owing to low linear correlation.

The parameters and correlation coefficients fitted by the simulation equations in Figure 7 are shown in Table S3. It was found that the Freundlich model agrees well with the experimental data, and the correlation coefficient $R^2$ is 0.972. It is concluded that the Zn$^{2+}$ adsorption process in the HFO produced by SACC is a multilayer adsorption behavior. When all of the active sites in the adsorbent are occupied by Zn$^{2+}$, the HFO adsorbent reaches a saturated adsorption of Zn$^{2+}$. Zn$^{2+}$ in wastewater is mainly removed through adsorption and co-precipitation.

The plot of ln $K_d$ and $1/T$ is shown in Figure 8, the changes of enthalpy and entropy are obtained from the slope and intercept and applying the Van ‘t Hoff equation (see Equation (12)). The positive values of enthalpy change indicate that the adsorption is an endothermic process. The negative values of Gibbs free energy change indicate that the adsorption of Zn$^{2+}$ on the HFO adsorbent is a spontaneous process. The positive values of entropy change indicate that the Zn$^{2+}$ adsorption probability of the interface between solution and adsorbent increases (the adsorption randomness at the solid–liquid interface increases). The elevation of temperature led to the increase of the Zn$^{2+}$ adsorption capacity in the HFO due to the amplification of pore volume and surface activation of the adsorbent.

**CONCLUSIONS**

The Zn$^{2+}$ removal from wastewater can be successfully applied by SACC technique. The optimum process conditions of SACC with iron electrodes for the Zn$^{2+}$ removal are $c_0 = 120$ mg·dm$^{-3}$, pH = 9, $j = 0.31$ A·m$^{-2}$, $t = 21.3$ min. Under the optimal process conditions, the Zn$^{2+}$ removal efficiency reached 98.80%, and the energy consumption was 1.147 kWh·m$^{-3}$. The flocculants produced by SACC have the characteristic of large specific surface area, meaning a high amount of Zn can be adsorbed on the surface of HFO produced by SACC process. The mechanism of
Zn$^{2+}$ adsorption was divided into two phase of Zn$^{2+}$ adsorption on HFO and then co-precipitation of adsorbed Zn$^{2+}$ and HFO. Zn$^{2+}$ adsorption behavior can be described by pseudo-second order kinetics and the Freundlich isotherm model. The Zn$^{2+}$ adsorption on the flocs produced by SACC from wastewater is an endothermic and spontaneous process.

**CONFLICTS OF INTEREST**

There are no conflicts to declare.

**ACKNOWLEDGEMENTS**

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


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