INSS Press Journal of Intelligent and Sustainable Systems

Article

Sustainable Resource Recycling of Pickling Bath Sludge into a High-Performance Erdite Adsorbent for Oxytetracycline Removal

Dandan Yang[1], Xin Lan[1], Wenjing Luo[1], Jiancong Liu[2,*], Wensheng Qin[3], Md. Shafiqur Rahman[3,4], Suiyi Zhu[1], Yu Chen[1,*]

[1] The 102-Joint Lab, Zhongkai University of Agriculture and Engineering, Guangzhou, China;

[2] Joint Lab for Wastewater Treatment, Changchun Institute of Technology, Changchun, China;

[3] Department of Biology, Lakehead University, Thunder Bay, ON, Canada;

[4] Department of Microbiology, University of Chittagong, Bangladesh.

Corresponding authors: Jiancong Liu (liujiancong0214@163.com); Yu Chen (chenyu202402@126.com)

Abstract

Pickling bath sludge, classified as a hazardous waste, is disposed of by landfill for decades. This study explores its resource utilization as an adsorbent material. The sludge primarily comprises $FeF_3 \cdot 2H_2O$ and Cr or Ni or Fe-bearing spinels. A multi-step processing strategy was developed: FeF_3 was first removed by NaOH washing to effectively recover F^-, followed by HCl leaching to generate a Fe-rich solution and a spinel-enriched residue. Direct hydrothermal treatment of the raw sludge and leaching residues with sodium sulfide at 160°C for 6h produced particles with low oxytetracycline (OTC) adsorption capacity (<250 mg/g). Conversely, the acid leachate (containing ~20 g/L Fe) was hydrothermally treated to synthesize erdite particles, which exhibited significantly higher OTC adsorption capacity (~2000 mg/g), approximately ten times greater than materials derived from the untreated sludge or residues. Mechanistic studies revealed that erdite undergoes spontaneous hydrolysis in aqueous solution to form Fe–S flocs with abundant sulfhydryl and hydroxyl groups, enabling strong coordination with OTC molecules. This work demonstrates a sustainable approach for converting pickling bath sludge into a high-performance adsorbent, offering both environmental remediation and sustainable waste management. Therefore, the OTC degrading bacterial candidate can be used on the surface of the constructed adsorbent for enhancing OTC adsorption.

Keywords: pickling bath sludge; waste reutilization; adsorbent; wastewater treatment; sustainability.

1. Introduction

Stainless-steel pickling is a surface-conditioning process that uses hot mixed acids, typically hydrofluoric acid (HF), hydrochloric acid (HCl) and nitric acid (HNO_3), and in some cases sulfuric acid (H_2SO_4) to remove surface defects associated with oxide scales [1, 2]. After pickling, the treated stainless steel can be fed into subsequent processes. During continuous operation of the pickling bath, large amounts of iron (Fe), chromium (Cr) and nickel (Ni) are dissolved into the hot acid and then progressively precipitate via fluoride reactions and/or crystallization pathways [3], leading to the formation of pickling bath sludge.

Therefore, this pickling bath sludge often contains residual acidity, fluoride and hazardous heavy metals include Cr and Ni, classified as hazardous waste [3]. The safe management of fluoride-rich wastes has therefore attracted sustainability-driven attention for decades. A common practice is to blend the sludge into cement–sand mortar to form cubic construction materials, followed by 28 days of water curing [4]. Other solidification or stabilization routes using asphalt, gypsum or limestone [5], resins, and related binders [6, 7] have also been explored to produce road-base materials, mine backfill materials and vitrified or glassy products, as part of sustainable resource management [8]. In addition, the sludge has been used as an additive in steel refining [9] due to its high Fe content and the presence of Cr and Ni at low dosages. The alloying elements of Cr or Ni may benefit strength for making stainless steel [10], although the high fluoride content remains a major drawback. From a sustainability standpoint, such 'utilization' approaches are essentially equivalent to final disposal and differ from the goal of recovering high-value products.

In contrast, reports on high-value recovery from pickling bath sludge are scarce. Literature searches on resource recovery often shift to a different waste stream in which sludge generated from pickling wastewater treatment mainly consists of CaF_2 and metal oxyhydroxides [11, 12]. Unlike wastewater sludge, the bath sludge is enriched in refractory Cr–Fe–Ni phases [13], including chromite-type spinels such as $FeCr_2O_4$ and $NiCr_2O_4$ [4], therefore, these phases are difficult to dissolve even under acidic conditions [14], creating a distinct challenge for efficient recovery from bath sludge. These spinels incorporate Cr in a stable trivalent oxide framework, rendering them highly resistant to dissolution, even under acidic conditions. However, the Cr(III) in these spinels can be oxidized to hexavalent chromium through calcination or roasting treatments. For example, roasting the spinels at 600–800°C with sodium carbonate converts the refractory chromium into soluble sodium chromate (Na_2CrO_4) [15], which can then be leached and purified for reuse in industries such as ceramics or alloy production. Herein, stainless-steel pickling bath sludge was treated by sequential leaching with water, alkaline solution, and acid. Moreover, the raw sludge, the leaching residues, and the leachates were further subjected to hydrothermal processing in the presence of sodium sulfide. The formation pathways and underlying mechanisms are discussed, and the resulting materials were evaluated for their application in wastewater treatment. In this research work, erdite the Fe–S flocs were constructed from pickling bath sludge, which has excellent adsorption capability of oxytetracycline (OTC); thus, it could be used for the removal of OTC from wastewater in an upcycling pathway.

The antibiotic oxytetracycline (OTC) is a common veterinary medicine, widely used for treating and preventing infectious diseases of animals [16]. China produces about 10,000 tons of OTC annually [17], and a large amount of OTC is exposed in the environment from animal excrement due to inadequate metabolism in animals, directly entering the aquatic environment through wastewater [18]. Therefore, the continuous release of OTC in the water environment creates antibiotic resistance and a harmful residual effect on the organisms of aquatic ecosystems [19]. The most frequently used veterinary antibiotics oxytetracycline (OTC), has adverse residual effects on aquatic environments; thus, an effective treatment method is immediately needed. Therefore, bioremediation of organic pollutants including OTC present in aquatic environment using microbial candidates has been gained attention to the researchers [20]. Consequently, several organic pollutants have a toxic effect on the microorganisms, moreover, some bacterial and fungal candidates are capable of utilizing these toxic pollutants includes OTC [21]. Thus, OTC utilizing bacterial strains could be used on the surface of newly constructed erdite adsorbent for bioconversion of OTC to facilitate more adsorption of OTC on erdite adsorbent. The adsorbent will entrap OTC within its pores, while microorganisms will degrade this antibiotic OTC in situ, thus, achieving biological regeneration of the adsorbent.

2. Materials and methods

2.1. Pickling bath sludge collection

The sludge was sampled from the bottom of a pickling bath at Hongze Stainless Steel Company (Wuxi, China). It was filtered using a frame filter, collected in bags, and stored in a designated hazardous waste facility. A portion was dried at 105°C for characterization, while the remainder was used directly without drying treatment.

2.2. Sodium sulfide treatment of the sludge

The pickling bath sludge was treated to produce SPs (Fig. 1). Briefly, 2.0 g of sludge was dispersed into 30.0 mL of water to form a suspension, then $Na_2S \cdot 3H_2O$ was added at an S/Fe molar ratio of 3.0 under stirring at 100 rpm. The resulting suspension was heated to 160°C for 6h, then cooled to room temperature. Subsequently, the suspension was centrifuged at 5500 rpm for 10 minutes to separate the supernatant from the blackish particles. The particles were then freeze-dried at −80 °C overnight. Control experiments were performed by varying the S/Fe ratio from 0 to 6.0. The resulting particles were designated as SPs.

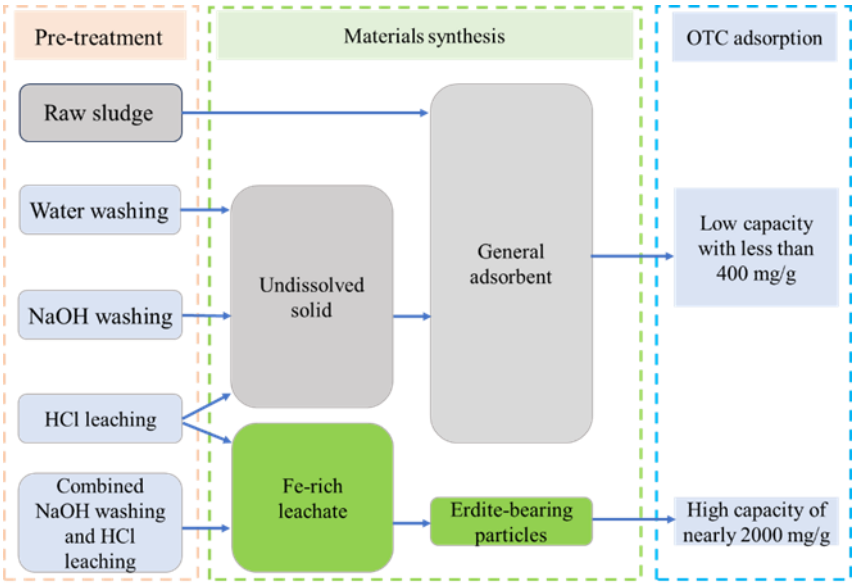

Figure 1. Illustration graph of treatment method for pickling bath sludge.

2.3. Sludge leaching by acid and alkaline solution

The sludge was leached sequentially with water and acid as follows: 4.0 g of sludge was dispersed into 20.0 mL of aqueous solution at a sludge-to-liquid ratio of 1:5 and stirred at 100 rpm for 2.0h. The suspension was then centrifuged at 5500 rpm for 5 min to separate the leachate from the undissolved residue. The water was replaced with 6.0 M HCl, and the treatment was repeated following the same procedure. Thus, the residues generated after water washing and acid leaching were subsequently treated according to the procedure described in Section 2.2. The resulting blackish particles were designated as SPs-water and SPs-HCl, respectively. However, in parallel, the sludge was leached with 1.0M NaOH solution as follows: 4.0 g of sludge was mixed with 80.0 mL of NaOH solution, heated to 80 °C under stirring at 100 rpm for 2.0h, and then cooled to room temperature. The suspension was centrifuged to separate the clear solution from the washed particles. The washed particles were then leached with 6.0M HCl using the same procedure described above to generate a leachate and undissolved residue.

The particles obtained from NaOH washing and from sequential NaOH washing and HCl leaching were further treated following the procedure described in Section 2.2, and the resulting adsorbents were designated as SPs-NaOH and SPs-NaOH/HCl, respectively. Moreover, the acid leachates were also treated following the procedure in Section 2.2, and the resulting adsorbents were named SPs-HCl-leachate and SPs-NaOH/HCl-leachate, respectively.

2.4. Oxytetracycline (OTC) adsorption experiment

The raw sludge and treated products were evaluated for OTC adsorption. Briefly, 10.0 mg of sludge was dispersed into 50.0 mL of 1.0 g/L OTC solution and stirred at 120 rpm. At predetermined intervals, 2.0 mL aliquots were withdrawn and analyzed. The adsorption capacity was calculated using Equation (1):

$$AC = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where, AC is the adsorption capacity (mg/g), t is the sampling time (min), C_0 and C_t are the OTC concentrations at the initial stage and at time t (min), and m is the mass of sludge (g). The adsorption performance of the prepared products was evaluated following the same procedure.

2.5. Characterization

The sludge, undissolved residues, and products were characterized by XRD, XRF, and SEM. The pH of the solution was measured using a pH meter, and metal ion concentrations were determined by ICP-OES. Fluoride concentrations were analyzed by IC, and OTC concentrations in solution were determined by HPLC. The hydrolysis performance of metallic ions in the leachate was simulated by using MEDUSA software (v1.0, KTH Royal Institute of Technology, Sweden). Moreover, the important lines in these plots were highlighted according to your suggestion.

3. Results and discussion

3.1. The sludge composition and its leaching

The pickling bath sludge was loose particles containing 30.5% water and could be readily filtered using a plate filter. After drying, its XRD pattern revealed sharp peaks of $FeF_3 \cdot 3H_2O$ and spinel peaks corresponding to magnetite and $NiFe_2O_4$ (Figure 2a). The XRF analysis showed the sludge contained 58.8% Fe, 25.2% Cr, 10.4% F, 3.4% Ni, and 0.6% Mn (Figure 2b). Notably, sharp peaks corresponding to Cr-bearing minerals were not observed in the XRD pattern, likely due to their overlap with the dominant peaks of Fe-rich spinel. Given Cr's trivalent oxidation state and atomic radius comparable to that of Fe, Cr likely substitutes for Fe within the Fe-rich spinel structure. [22].

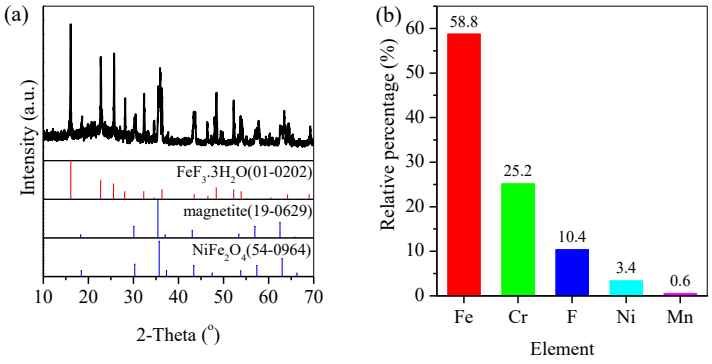

Figure 2. (a) XRD pattern and **(b)** XRF results of raw sludge

The sludge was washed with water and NaOH solution, separately. Water washing yielded a scrubbing solution containing 5.9 g/L fluoride and 0.2 g/L Ni (Figure 3a). NaOH washing produced a solution with 14.9 g/L fluoride, while the Ni concentration remained below the detection limit.

Direct dissolution of the sludge in 6.0M HCl resulted in a leachate containing 1.5 g/L fluoride, 28.0 g/L Fe, and low concentrations of Cr and Ni. The lower fluoride concentration compared to the NaOH washing solution was attributed to the formation of hydrofluoric acid during acid leaching, which subsequently volatilized [23].

Following NaOH washing, the resulting solid residue was further leached with 6.0M HCl. The resulting acid leachates contained approximately 20.0 g/L Fe, 0.4 g/L Cr, 0.8 g/L Ni, and only 0.05 g/L fluoride (Figure 3a). These results demonstrated that NaOH washing effectively removed fluoride from the sludge, thereby enabling sustainable fluoride recycling. The residue consisted of spinel particles of magnetite and $NiFe_2O_4$ (Figure 3b). Therefore, the XRF analysis of this residue revealed compositions of 44.0% Fe, 52.1% Cr, 0.6% Ni, and 0.9% Mn (Figure 3c), confirming that $FeF_3 \cdot 3H_2O$ was completely removed during NaOH washing, while the spinel particles remained unchanged.

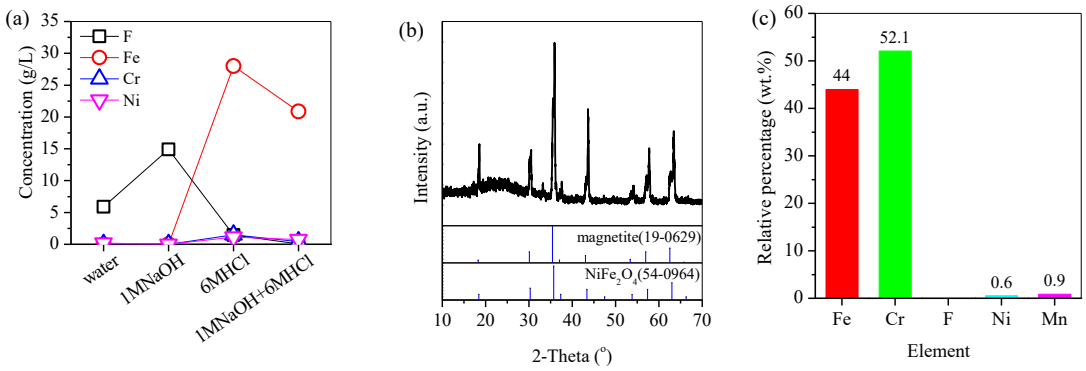

Figure 3. (a) Leaching test, **(b)** XRD patterns and **(c)** major composition of undissolved particles generated by acid leaching.

The F^- content in the raw sludge was 10.4%, primarily present as $FeF_3 \cdot 3H_2O$. After water washing, the F^- content in the undissolved particles decreased to approximately 6.4%. Subsequent NaOH washing further reduced it to 0.025%, and HCl leaching brought it nearly to zero. This confirms that NaOH washing efficiently removes fluoride from the residue by converting fluoride-bearing $FeF_3 \cdot 3H_2O$ into iron oxyhydroxides, thereby supporting the sustainable utilization of solid waste.

3.2. Sludge conversation and its oxytetracycline (OTC) adsorption performance

3.2.1. Sludge and its conversion

The sludge underwent hydrothermal treatment with or without sodium sulfide, resulting in particles with an adsorption capacity of less than 250.0 mg/g OTC (Figure 4a). Correspondingly, approximately 2.0 g/L fluoride appeared in the treated supernatant without sodium sulfide, which increased to higher levels when sodium sulfide was added (Figure 4b), revealing enhanced fluoride leaching in alkaline solution. However, when the sludge was calcined at 500°C for 1h and subsequently treated with sodium sulfite, the resulting particles demonstrated a small adsorption capacity of less than 100.0 mg/g OTC (Figure 4a), and the supernatant contained only 0.2 g/L fluoride (Figure 4b). These results demonstrated the significant loss of fluoride and spinel formation occurred during sludge calcination.

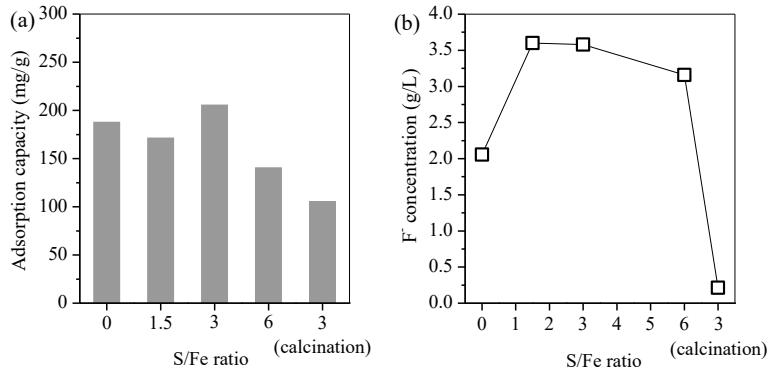

Figure 4. (a) adsorption capacity of OTC onto treated sludge, and **(b)** fluoride concentration in the supernatant.

3.2.2.Residual and its conversion

The pickling bath sludge was first washed with water and then treated by adding sodium sulfide at molar ratios ranging from 2.0 to 6.0. However, the resulting particles exhibited low adsorption capacity for oxytetracycline (OTC) which was below 250.0 mg/g (Figure 5a), despite fluoride concentrations in the supernatant being lower than 0.1 mg/L (Figure 5b).

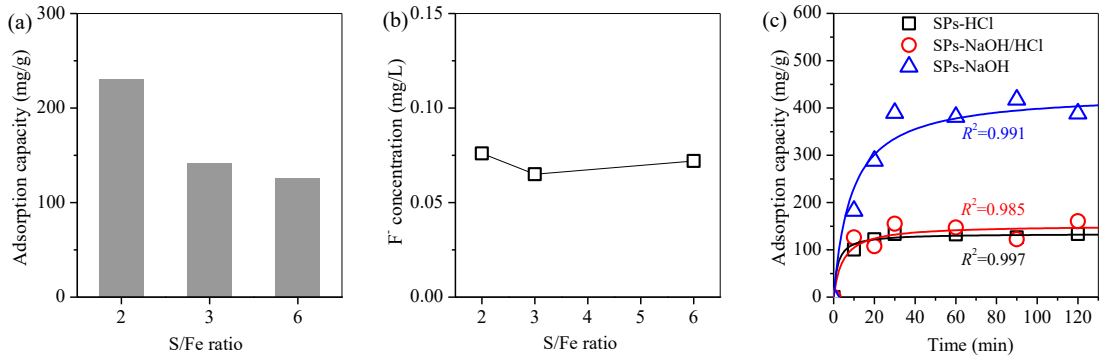

Figure 5. (a) adsorption capacity of OTC onto adsorbents generated using washed sludge, **(b)** fluoride concentration in the treated supernatant, **(c)** adsorption capacity of OTC onto adsorbents generated by using acid leached sludge.

After acid leaching, the generated residues were further treated by adding sodium sulfide, and the resulting particles demonstrated the low adsorption capacities of less than 150.0 mg/g OTC (Figure 5c). In contrast, the residue obtained after NaOH washing was similarly treated, and the resulting particles showed an adsorption capacity of approximately 400.0 mg/g OTC (Figure 5c), substantially higher than those treated after acid leaching.

3.2.3.Acid solution utilization

Two acid leachates were obtained: one from direct HCl leaching and the other from NaOH washing followed by HCl leaching. Both leachates were hydrothermally treated with sodium sulfide to produce SPs-HCl-leachate and SPs-NaOH/HCl-leachate. Notably, SPs-HCl-leachate and SPs-NaOH/HCl-leachate exhibited OTC adsorption capacities of 1890.0 and 2337.0 mg/g, respectively, which are approximately twenty times higher than those of materials prepared directly from the sludge and its leaching residues (Figure 6a).

It is noted that the acid leachate contained 1.5 g/L F^- before treatment (Figure 6a), but only 0.01 g/L F^- after treatment. This indicated that F^- was consumed during the formation of SPs-HCl-leachate and likely reduced its adsorption capacity.

SPs-NaOH/HCl-leachate showed the highest OTC adsorption capacity, and it was further characterized by XRD. The XRD pattern exhibited characteristic peaks of erdite (Figure 6b). The initial Fe concentration in the leachate was approximately 20.0 g/L, but after treatment it decreased to below the detection limit, indicating incorporation of Fe into the erdite phase. After adsorption, the erdite peaks disappeared and only sulfur peaks remained (Figure 6c), suggesting that erdite hydrolyzed during use and played a key role in OTC adsorption, in a sustainably functioning adsorption–conversion process.

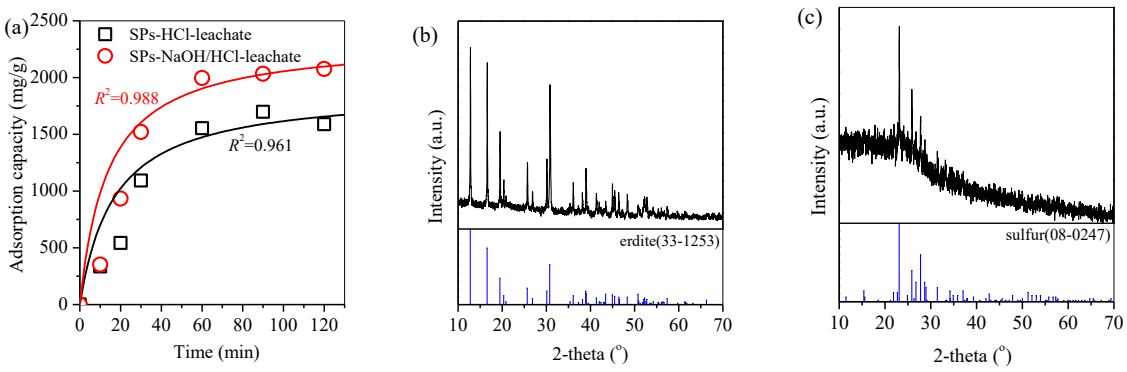

Figure 6. Adsorption capacity of OTC onto adsorbents prepared by using acid leachates, XRD patterns of SPs-NaOH/HCl-leachate **(a)** before and **(b)**, **(c)** after use.

3.3. Leaching and conversion mechanism

The sludge mainly comprised $FeF_3 \cdot 2H_2O$ and spinel minerals such as magnetite and $NiFe_2O_4$. The Cr was also enriched in the sludge, mainly present as spinels (e.g., $NiCr_2O_4$ and $FeCr_2O_4$), where XRD reflections overlapped with those of magnetite and $NiFe_2O_4$, and could not be distinguished directly. During direct calcination, $FeF_3 \cdot 2H_2O$ was dehydrated to FeF_3 and could further react with Ni/Cr-bearing hydroxides, contributing to spinel formation [24].

When the sludge was washed with water, $FeF_3 \cdot 2H_2O$ hydrolyzed to release F^- and formed Fe hydroxides (Figure 7a and Figure 8), whereas the spinel $NiFe_2O_4$ remained unchanged (Figure 7b). As hydrolysis proceeded, the pH of the washing water gradually decreased to below 7.0, which suppressed further hydrolysis [25]. Consequently, some $FeF_3 \cdot 2H_2O$ remained in the washed residue even after multiple

washing cycles, because Cr(III) has a similar ionic radius to Fe(III) and it could also form CrF_3(Figure 7c), although Cr was mainly incorporated into spinel phases [26]. When the sludge was washed with NaOH solution, the H^+ produced during FeF_3 hydrolysis was neutralized, accelerating conversion to free $F^-$and iron hydroxides (Figure 8). Upon heating, iron hydroxides and Ni/Cr hydroxides could further transform into spinels [27]. In contrast, HCl leaching dissolved $FeF_3·2H_2O$ and Ni/Cr hydroxides to generate a metal-rich solution. During acid leaching, HF could form and volatilize, resulting in a relatively low F^- concentration in the leachate.

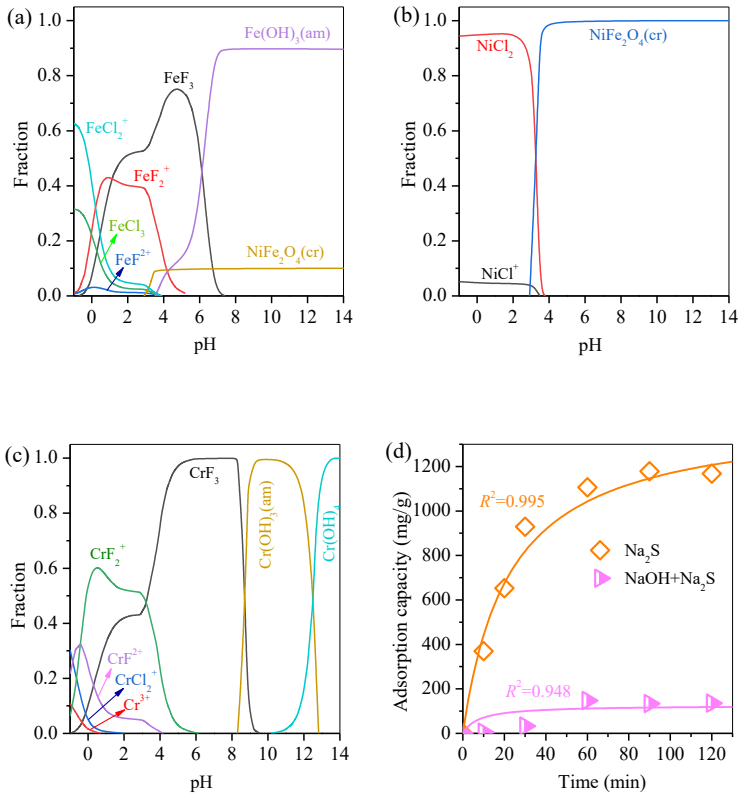

Figure 7. Hydrolysis precipitation of (a) Fe, (b) Ni and (c) Cr in the presence of F^- and Cl^-, and (d) adsorption performance of OTC by materials prepared using $FeF_3·2H_2O$.

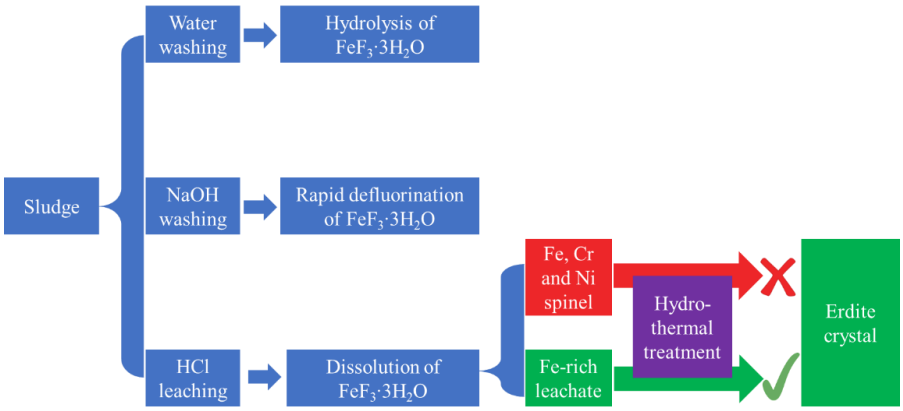

Figure 8. Entire process of sludge leaching and its conversion performance

The acid leachate was rich in Fe and was used for erdite synthesis via a hydrothermal route, which typically proceeds in three steps. First, Fe hydrolyzes to form flocs in alkaline solution [28]. Second, these Fe-bearing flocs partially dissolve to release $Fe(OH)_4^-$, which reacts with $HS^-$to form species such as $Fe(OH)_3HS^-$and $Fe(OH)_2(HS)_2^-$ [29]. Third, two $Fe(OH)_2(HS)_2^-$ units polymerize to form $FeS_2Fe(OH)_4^{2-}$, releasing H_2O into solution [30]. With continued polymerization, $(FeS_2)_n^{n-}$chains are formed, and their negative charge is balanced by Na^+ [31, 32], yielding erdite rods. This supports sustainability by effective Fe conversion under alkaline condition.

The raw sludge and undissolved particles were also treated hydrothermally. Spinel particles, abundant in the sludge and leaching residues, remained stable during hydrothermal treatment. However, the hydrothermal transformation of $FeF_3 \cdot 2H_2O$ in alkaline solution remains unclear. As shown in Figure 7d, particles produced with only sodium sulfide exhibited a high OTC adsorption capacity of 1433.0 mg/g, comparable to materials derived from Fe oxyhydroxides, indicating erdite formation. In contrast, in the presence of NaOH, the products showed a much lower adsorption capacity (126.0 mg/g), close to that of materials prepared from raw sludge or leaching residues. FeF_3 was decomposed in NaOH solution at room temperature, but remained stable under the hydrothermal conditions. However, in the absence of NaOH, a direct reaction between FeF_3 and HS^- occurred at high temperature, leading to the formation of Fe-S intermediates that are involved in erdite rods synthesis. Notably, this reaction was rapid at the initial stage, but it ceased when a large amount of free OH^- began to accumulate. This suggests that NaOH inhibited the conversion of $FeF_3 \cdot 2H_2O$ to erdite.

Therefore, the OTC adsorption on spinels is very low, likely occurring mainly through the coordination of amino or hydroxyl groups of OTC to the defective sites on the spinel surface [33, 34]. Moreover, when OTC was introduced into an erdite-containing solution, a different process dominated. First, erdite spontaneously hydrolyzed to form Fe–S flocs rich in sulfhydryl and hydroxyl groups [35]. Second, sulfhydryl groups coordinated more strongly with cationic amino groups of OTC compared to those of hydroxyl groups [36]. Third, as hydrolysis progressed, these flocs captured OTC and subsequently polymerized or aggregated to precipitate, resulting in high OTC removal. In addition, a small fraction of HS was oxidized by dissolved oxygen to form elemental sulfur, consistent with sulfur peaks observed in the corresponding XRD patterns.

Building on the adsorption–precipitation mechanism of OTC driven by erdite hydrolysis, we propose an integrated adsorption–biodegradation conceptual framework. In this sustainability-enhanced remediation approach, a potential OTC-degrading bacterial candidate is coupled with the high-performance adsorbent. Due to its large surface area and well-developed pore structure, the adsorbent offers abundant attachment sites that promote microbial adhesion and colonization on the erdite-based surface, mirroring the supportive role of biochar [37]. Within this configuration, the adsorbent serves as a favorable immobilization carrier while simultaneously sustaining OTC capture via coordination and flocculation, thereby enabling a synergistic removal pathway.

However, this acid-washed sludge-derived material still contains multiple metals (including Ni, Cr, and Fe), which may inhibit the growth of freely suspended bacterial strains. Immobilized bacteria and

biofilm-forming microorganisms can better withstand such stress by buffering the local toxicity of metal ions and improving tolerance. Moreover, the immobilized microbial system can adapt to adverse conditions, such as varying pH and heavy-metal loads, as well as co-existing toxic pollutants including OTC [38]. Therefore, for organic-pollutant treatment in aquatic environments, this immobilized microbial technology is widely considered due to its excellent environmental adaptability [39]. In practice, immobilized bacteria can further utilize the OTC accumulated on the adsorbent, complementing adsorption and advancing overall OTC removal.

Consequently, it has been proved that many bacterial strains could efficiently degrade OTC from water and produce no or less toxic products [28]. It has been reported that an OTC-degrading bacterial strain *Arthrobacter nicotianae* OTC-16 utilized 98.5% of OTC after 8 days in optimized culture conditions and converted OTC into low-toxicity metabolites [21]. Moreover, the bacterial isolates *Pseudomonas* sp. and *Mycolicibacterium* sp. exhibited 60.0% and 92.8% of OTC removal activity, respectively [20]. Thus, the OTC utilizing bacterial strains could be introduced on the adsorbent for increasing adsorption of OTC.

3.4. Potential application

The sludge contained F^- and heavy metals (Cr and Ni) and was classified as hazardous waste. To enable sustainable waste management, this hazardous waste was converted into general waste by removing F^-, Ni, and Cr. In this study, alkaline washing proved highly effective for F^- removal, and the alkaline solution could be regenerated with F^- recovered as NaF through electrolysis. Washing with NaOH reduced its weight by only about 1%, consistent with the conversion of FeF_3 to iron oxyhydroxides. However, after HCl leaching, the weight loss reached 72%, which aligns with the dissolution of Fe-bearing oxyhydroxides. The residual solids contained spinel phases such as magnetite, $NiFe_2O_4$, and Cr-containing compounds [29]. The resource utilization of spinel residues therefore remains a significant challenge.

Following F^- removal, Fe hydroxides remained in the residue and were readily dissolved in acid to generate a Fe-rich leachate. The Fe in this leachate could be easily converted to Fe oxyhydroxides and subsequently transformed into erdite crystals via hydrothermal treatment. Therefore, as an efficient flocculant, the erdite functions are readily hydrolyzed to form flocs capable of removing diverse contaminants, including OTC-type organic pollutants [40], heavy metals [41, 42], and various anions [43]. This strategy provides a novel pathway for resource utilization of Fe derived from hazardous sludge, effectively transforming a waste stream into a valuable water treatment material.

4. Conclusion

This study presented a sustainable strategy for valorizing hazardous pickling bath sludge into valuable functional materials for wastewater treatment. The sludge, primarily composed of $FeF_3 \cdot 2H_2O$ and Cr/Fe/Ni-bearing spinels, was processed through a sequential separation and conversion approach.

Initial NaOH washing effectively removed fluoride (from 10.4% to 0.025%), with the potential for its recovery. Subsequent HCl leaching generated a Fe-rich leachate ($\approx$20 g/L Fe) and a Cr/Fe/Ni spinel

residue. While hydrothermal treatment of raw sludge yielded materials with limited OTC adsorption (<250 mg/g), the Fe-rich leachate was successfully converted into erdite particles via hydrothermal synthesis. These erdite particles exhibited an outstanding OTC adsorption capacity of ≈2000 mg/g, which was over ten times higher than materials derived from direct sludge treatment. Mechanistic analysis revealed that erdite's high performance stems from its hydrolysis in aqueous solution, forming Fe–S flocs rich in sulfhydryl and hydroxyl groups that serve as strong coordination sites for OTC molecules.

Overall, the proposed separation–conversion framework enables sustainable resource utilization of hazardous pickling waste while achieving superior adsorption performance. The integrated process not only addresses iron valorization but also offers a pathway for fluoride recovery. The residual spinel phases, though separated, warrant further investigation for comprehensive utilization.

Acknowledgement

This work was supported by National Natural Science Foundation of China (No. 52370158 and 52470138), and the Science and Technology Program of Jilin Province (Grant No. 20240304153SF).

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