

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Magnetic Separation of Impurities from Hydrometallurgy Solutions and Waste Water Using Magnetic Iron Ore Seeding

Haisheng Han, Wenjuan Sun, Wei Sun and Yuehua Hu

Abstract

The removal of iron ion from leaching solution is critical for the recovery of value metals, with the method of choice commonly being crystallization (precipitation). This paper summarized the new improvements in iron removal by precipitation methods in recent years and proposed a novel process, magnetic seeding and separation. The new process can promote iron precipitate aggregation and growth on the surface of the magnetic iron ore seeds. A core-shell structure was formed of iron precipitate and magnetic iron ore seeds, which can be magnetized and coalesced in magnetic field, accelerating the solid-liquid separation. The efficient magnetic flocculation and separation offset the poor settleability and filterability of the residues, contributing to the development of the hydrometallurgy process. Moreover, magnetic seeding and separation was also used for the removal of organic and inorganic contaminants from wastewater, significantly improving the purification efficiency. Therefore, iron ore not only played an important role in mining and steel manufacture, but also can be used to solve some problems in crossing fields.

Keywords: leaching solution, goethite process, iron removal, magnetic seed

1. Introduction

Iron is one of the most abundant elements in the earth's crust. It always coexists with metals in the ore, mainly exists in the form of hematite, magnetite and muscovite on the surface of particles or in the inclusions inside crystals [1]. In hydrometallurgy, iron, although is converted into insoluble precipitates and removed in advance by sulfation roasting, soda roasting, acid leaching, etc. during ore pretreatment, still inevitably goes to the aqueous solution with the dissolution of the target metal during the leaching process [2–4]. The classical methods for removing iron in the leaching solution are precipitation, extraction, ion exchange, displacement, and electrowinning [4]. The commonly used method is the precipitation method, which separates iron ions by converting to iron precipitation compounds. According to the different iron precipitation compounds, it can be divided into jarosite [5–6], hematite [7], iron(III) oxide-hydroxide [8] and goethite [9–10] method, etc. The jarosite method produces a large amount of low-grade iron-bearing slag in the application, which is difficult to handle, consumes a large amount of sulfate, and

causes certain environmental problems [5–6]; the hematite method needs to be carried out under high temperature and pressure, which consumes large energy and high CAPEX (capital expenditure) [7]. The filtration efficiency of $\text{Fe}(\text{OH})_3$ colloid precipitation method is low, and it is easy to adsorb a large amount of other valuable metals, causing large metal loss [8].

The goethite method is widely used in hydrometallurgical plants for zinc, copper and nickel as the main process for removing iron because of its low CAPEX and environmentally friendly products [9–10]. In order to ensure the effect and efficiency of iron removal, the goethite process must strictly control the concentration of Fe^{3+} below 1 g/L, and thus developed the two commonly used processes - VM method and EZ method [8–9, 11]. The former firstly reduces all the iron ions to Fe^{2+} , and then slowly oxidizes the Fe^{2+} to Fe^{3+} under hydrolysis conditions to control the content of Fe^{3+} [9], and the latter slowly adds the concentrated pressure leachate containing Fe^{3+} in the precipitation vessel with addition rate of less than the Fe^{3+} hydrolysis rate, thereby forming goethite precipitation [11]. The pH in goethite process is common lower than 4.0, and calcium hydroxide or calcium carbonate is usually used as neutralizer, which will result in a large amount of calcium sulfate mixed with the goethite residue [12]. These mixed residues reduce the filtration efficiency and cause the loss of valuable metals such as Zn and Ni [5, 13–14]. In addition, the residue mixture accumulated in the tailings pond contains heavy metals such as Pb, As, and Cr, which causes pollution of local water and soil. Therefore, improving filtration performance and reducing the loss of valuable metals are two problems that need to be solved urgently in the traditional goethite precipitation method.

This article summarizes the new improvements in iron removal by precipitation methods in recent years, and on this basis, proposes a novel iron removal process - magnetic seeding and separation. A core-shell structure is formed by precipitating and growing iron on the magnetic seeds surface, and achieves high-efficiency solid-liquid separation by magnetic separation. The new process remarkably reduces the loss of valuable metals in iron removal. Magnetic seeding and separation processes have not only been successfully used in the removal of iron from hydrometallurgical leachate, but also shown good application prospects in wastewater and soil pollution treatment.

2. Iron removal in nickel and zinc leaching solution

2.1 Magnetite precipitate process

Magnetic flocculation and separation based on the magnetic difference of materials can easily separate magnetic solids from mixtures. It shows higher selectivity and efficiency than centrifugation and filtration, and has been widely used in water treatment, biotechnology and minerals separation [15–18]. As is shown in **Figure 1**, Han et al. [3] studied the feasibility of magnetite precipitation in the hydrometallurgical nickel leaching solution. Under lower oxidation potential, at pH 2.0–2.2 and 90–100°C, the iron ions in the leachate may slowly oxidize and partially precipitate in the form of magnetite. Magnetic flocculation and separation can effectively separate the precipitate from the solution. Unfortunately, the iron precipitation from solution is still dominated by goethite, the magnetite composition is relatively small, and it is difficult to truly achieve effective magnetic separation in industrial applications. But this research of magnetite process of iron removal provides other new ideas of magnetic separation.

2.2 Induced crystallization goethite process

The goethite process can be divided into four stages: (a) hydrolysis to monomers and dimers; (b) the reversible stage involving rapid growth to small polymers; (c) formation of slowly reacting large polymers; and (d) precipitation of a solid phase [19–20]. The goethite precipitation system is a complex system, and the presence and content of different components and iron phases have a greater impact on the precipitation and filtration performance of goethite. As shown in **Figure 2**, the pH and temperature conditions of the sulfate-containing solution determine the existence and content of different iron phases such as hematite, goethite, iron hydroxide and hydroxyl salt [21]. The goethite residues that cause

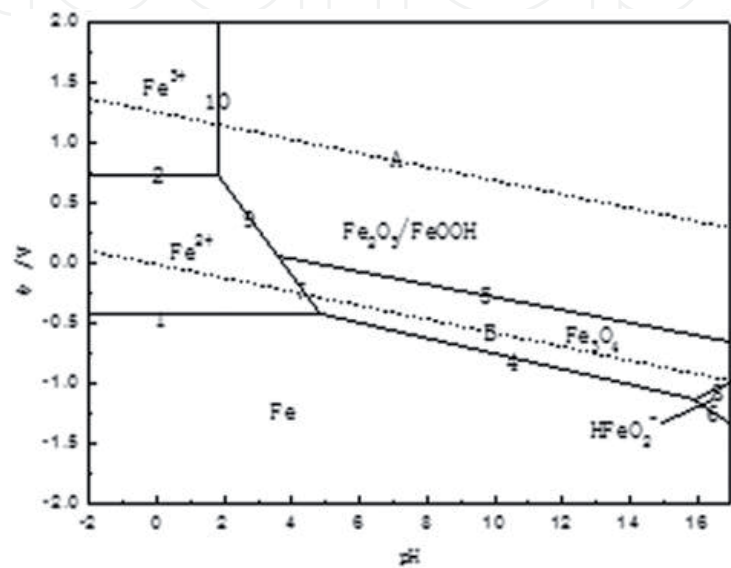


Figure 1.
Potential/pH diagram for Fe-H₂O system at 100°C.

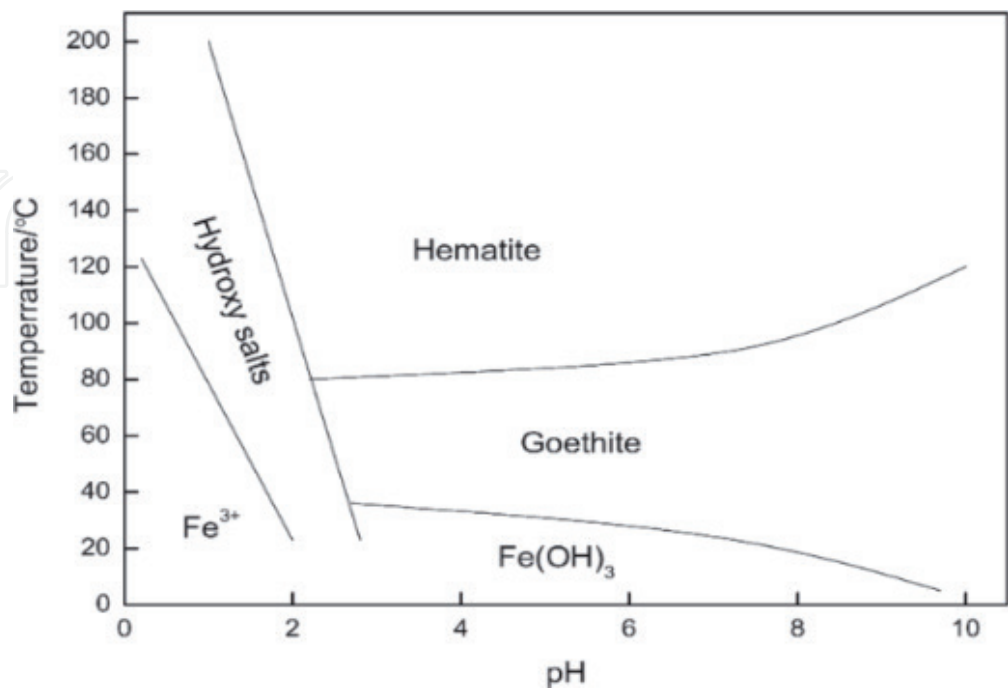


Figure 2.
Temperature and pH conditions for the precipitation of hematite, goethite, ferric hydroxide, and hydroxy salts (including jarosites) from 0.5 M ferric sulfate solution [21, 23].

filtration difficulties and metal loss are composed of amorphous iron phase, six-line ferrihydrite, poor crystalline goethite, solid solution jarosite phase and silica [2, 22]. Therefore, the crystallinity, size and content of the goethite particles can be controlled by adjusting the pH, thereby improving the separation performance and the loss of valuable metals.

Yue and Han [23] study that as the pH value decreases from 5.0 to 2.0, as shown in **Figure 3**, the crystallinity of goethite decreases, the goethite particles tend to agglomerate, the particle size increases significantly, and the filterability of the precipitate improves. Nickel is lost in the iron precipitate by being incorporated into the crystal lattice and adsorbed on the surface of the goethite particles, and the nickel adsorption loss are related to the specific surface area of the goethite particles. When goethite is in an intermediate transition state at low pH (2.5–3.3), which is between the crystalline state and the colloidal state, the loss of nickel is the least. However, the improvement by only adjusting the pH of the goethite precipitation process is minimal. Chang et al. [24] carefully reduced the pH from 4.0 to 2.5, and the loss of nickel is only reduced by about 10% in the iron precipitation. Moreover, it is not realistic to achieve such detailed condition control in actual industrial applications.

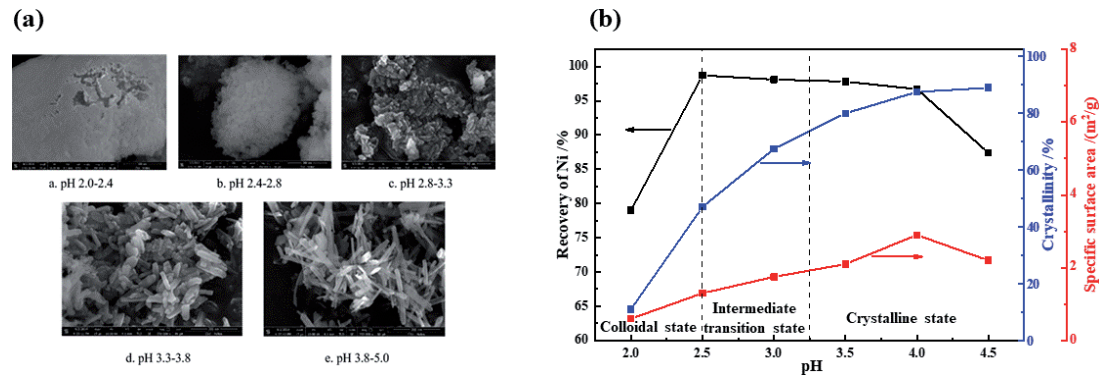


Figure 3. (a) SEM images of the goethite precipitate at different pHs and (b) pH effect for the nickel loss, the crystallinity, and the specific surface area of the precipitate [23, 25].

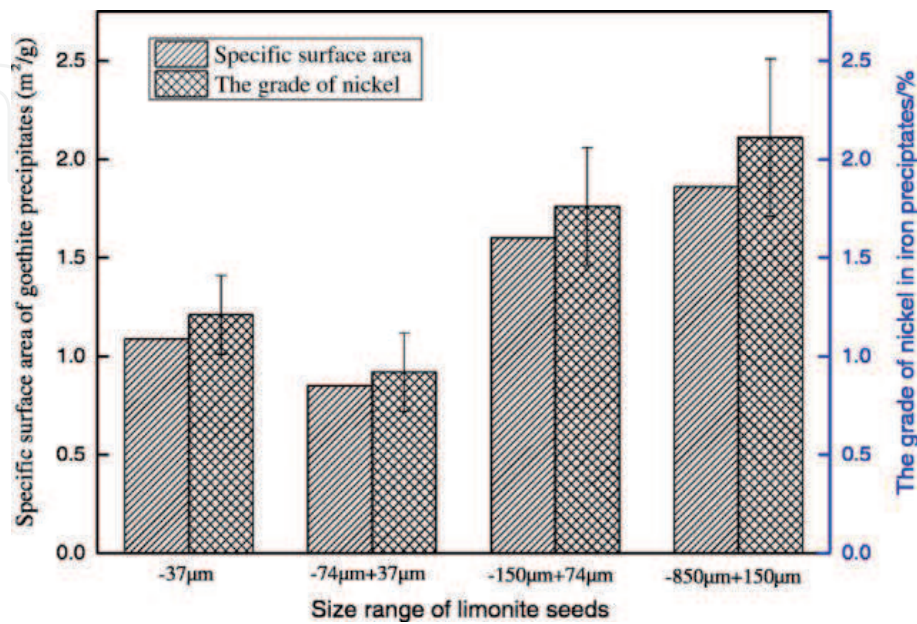


Figure 4. The specific surface area and the nickel grade of iron precipitates with limonite seeds in different size ranges (2 g/L limonite seeds, pH 2.1–2.5, 85°C) [30].

The traditional goethite precipitation method needs to overcome high barriers to the formation of crystals, and often requires a few days of reaction time. The amorphous iron phase appears at this stage, making precipitation separation difficult. Seed induced crystallization can make crystals precipitate and crystallize from the solution at lower solution saturation, pH value and temperature, and has been widely used in the preparation and production of drugs and nanomaterials [26–29]. Han [30] choose natural limonite as the seed crystal of goethite and induce crystallization to improve the problem of poor filterability at the low pH goethite precipitate. As is shown in **Figure 4**, by adding limonite seeds, the particle size of the goethite precipitate is significantly increased. The goethite particles in the particle size range of 37–74 μm have the largest yield and the smallest specific surface area, which can result iron precipitates with a nickel grade of <1%. However, the reduction of metal loss and improvement of filterability are difficult to achieve at the same time by pH control and induced crystallization, one of them must be sacrificed. The intermediate transition state goethite with good filtration performance and minimum metal loss is difficult to accurately induce formation in the actual field industry. It is a need to find other ideas to achieve qualitative progress.

3. Magnetic iron seeding and separation

Han et al. [25, 31–32] combined seed induced crystallization and magnetic separation, and proposed a novel magnetic seeding and separation process, as shown in **Figure 5**. Before the iron is precipitated as goethite, fine-grained maghemite or magnetite particles are added to the leaching solution to make the goethite precipitate and grow on the surface of the magnetic particles, thereby avoiding mixing with the calcium sulfate precipitation in the solution. The iron precipitates on the surface of the goethite to form large magnetic particles with a core-shell structure, and the precipitates are efficiently settled and separated by magnetic separation. The results show that the iron content in the dry iron residue is more than 52% and the Ni content is less than 0.6%, which can be used in industrial applications to deal with a large amount of iron precipitation. After the calcium sulfate precipitation is roasted, 99% of S and As can be removed, and the roasting residue can be respectively used as raw materials for ironmaking and building materials.

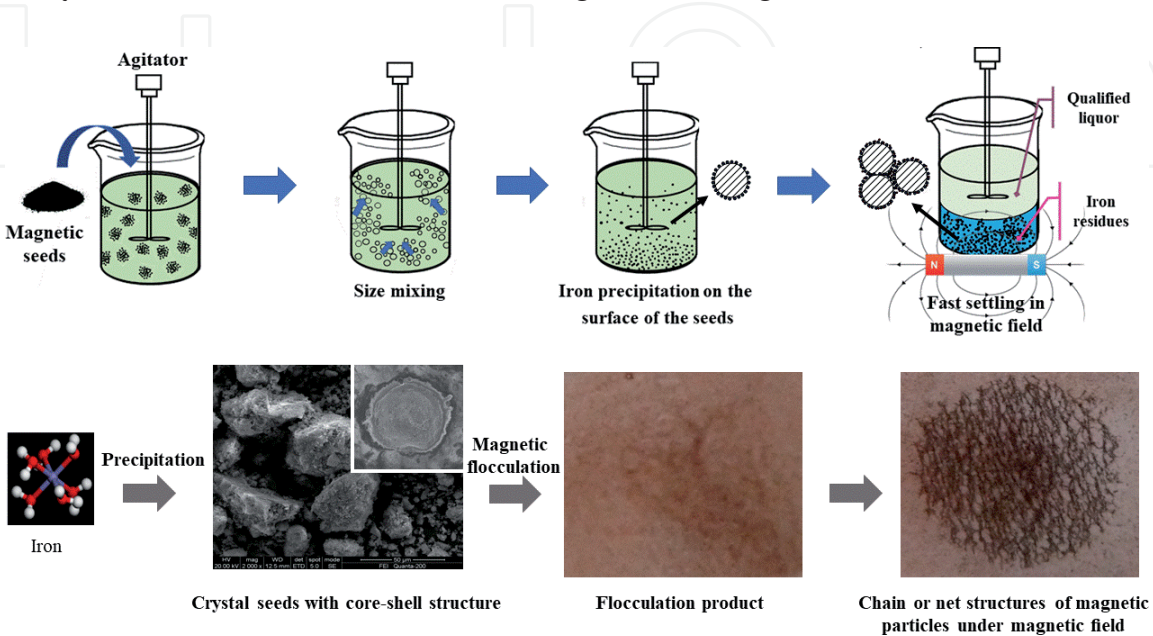


Figure 5.
The process of iron precipitation on the magnetic seeds and the magnetic flocculation in magnetic field [3, 25].

Yue et al. [31] applied magnetic iron seeding and separation to separate goethite from calcium sulfate in zinc leaching with maghemite fine particles as carrier. As is shown in **Figure 6**, the magnetic goethite-maghemite aggregates were separated effectively from calcium sulfate precipitates by magnetic drum separator, and 90% of Fe and Ca is respectively recovered in two corresponding products. Roasting goethite precipitate with coal powder under the optimum conditions removed 99% of S and As. Goethite products can be directly used in the ironmaking industry, and calcium sulfate precipitation can also be used to produce cement and building materials.

Yue et al. [32] establish the surface complex and precipitation model of goethite on magnetite and maghemite magnetic nanoparticles, as shown in **Figure 7**. The formation of Fe (III) surface complexes are directly related to the nucleation and

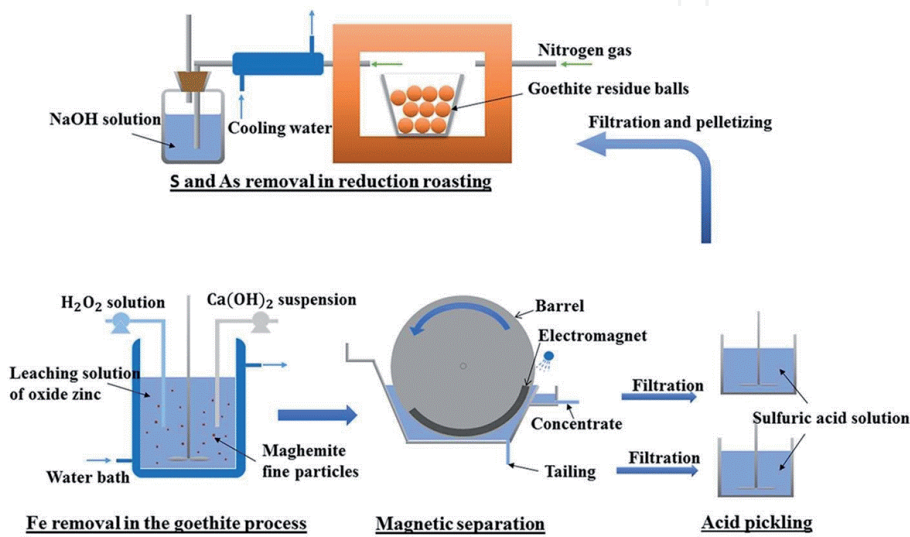


Figure 6. Schematic illustration of magnetic separation and production of desired goethite and gypsum product [31].

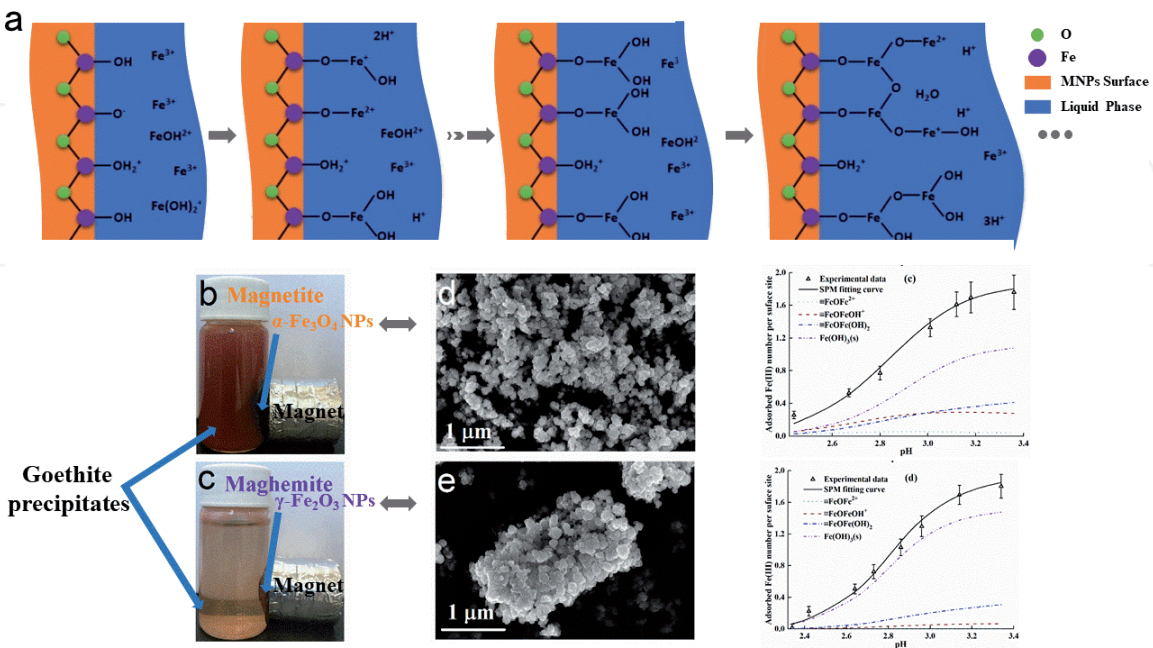


Figure 7. Surface precipitation model modeling (a) of Fe^{3+} adsorption/precipitation on magnetite and maghemite with corresponding magnetic separation of goethite, images of the suspensions in a magnetic field with 2 g/L (b) magnetite and (c) maghemite NPs, and SEM images of goethite precipitates with (d) magnetite and (e) maghemite NPs [32].

precipitation of goethite on the solid surfaces of the two magnetic nanoparticles. The more polynuclear surface complexes produced on the particle surface, the more precipitation of heterogeneous forms. Fundamentally, it is possible to screen out the best material as the crystal nucleus to separate goethite from calcium sulfate or other heterogeneous precipitation.

4. Application and prospect

4.1 Recycling Fe and Cr in Cr-bearing electroplating sludge

The Cr-bearing electroplating sludge is produced from the treatment of Cr wastewater and metallurgical processes [33–36]. It contains excessive amounts of heavy metals, such as Cr, Fe, Ni, Cu, Pb and Zn, or potential dioxin pollutants [37–38], therefore must be treated before stacking. Many methods have been applied to recover Cr from the acid leaching solution of electroplating sludge, such as electrochemical precipitation (ECP) [39], selective extraction [35, 40], adsorption or biosorption [41–44] and Cr-Fe coprecipitation [45–48]. Compared with other methods, recovering Cr by Cr-Fe coprecipitation is simple, economical and practical for industrial applications. In addition, the advance coprecipitation of Fe and Cr can avoid their interference on the recovery of Ni, Cu and Zn.

Yue et al. [49] use the novel magnetic seeding and separation process to recover Cr(III) and Fe(II) synchronously by forming the Cr(III)-Fe(III) coprecipitates on the surface of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) fine particles. The active hydroxide radicals on the surface of magnetic seeds induce the nucleation and growth of goethite, which results in enhanced Cr(III)-Fe(III) coprecipitation. As shown in **Figure 8**, the maghemite particles, served as the crystal nuclei, could induce the formation of the core-shell structured Cr(III)-Fe(III) coprecipitates on its surface and accelerate the sedimentation of the coprecipitates in the magnetic field. The results of the two-stage coprecipitation showed that the total recoveries of Cr and Fe were 96.17 and 99.39%, respectively, and the grades of Ni, Cu, and Zn in the precipitates were 0.41, 0.38, and 0.22%, respectively. The obtained coprecipitates can be recycled as the feed material of chromium smelting after heat treatment. This method is simple and efficient for high-concentration Cr^{3+} solution treatment, which is beneficial for the sustainable development of resources and environment.

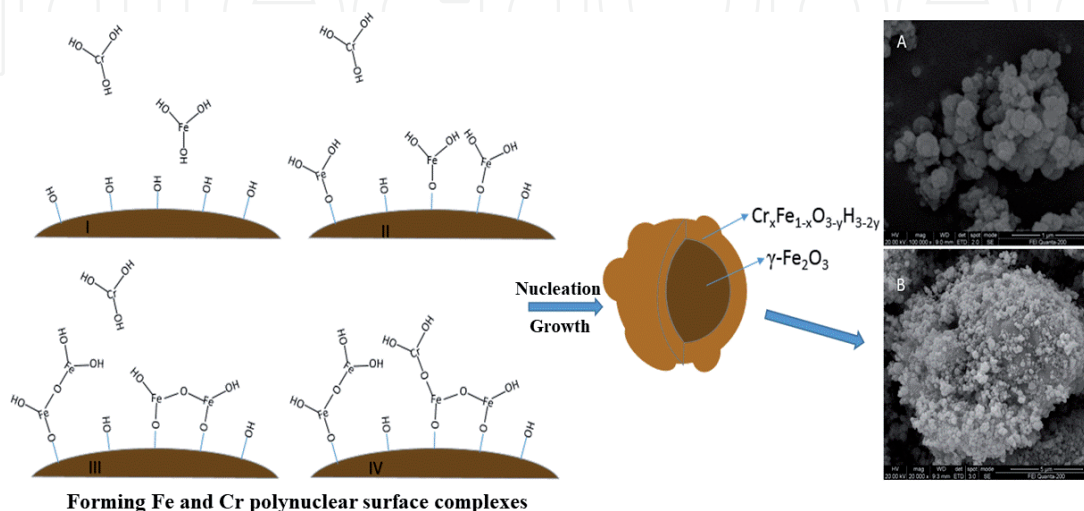


Figure 8. SEM images of the Cr(III)-Fe(III) coprecipitates without maghemite fine particles (a) and with maghemite fine particles (b), respectively; scheme (c) of the formation of $\gamma\text{-Fe}_2\text{O}_3/\text{Cr}_x\text{Fe}_{1-x}\text{OOH}$ with core-shell structure [49].

4.2 Removal of As in arsenic alkali residue

Arsenic (As) is contained in most metal deposits, and therefore a large amount of arsenic-containing wastewater, flue gas and residues will be produced in mineral processing and smelting, posing a huge threat to the environment [50–52]. Commonly used methods for removing arsenic from solution include precipitation, electrocoagulation, ion exchange, membrane technology and adsorption [53–56]. In order to remove arsenic and recover valuable metals at the same time, these methods all require acid leaching of the waste, which will produce highly toxic and deadly arsine gas [54, 57]. As is shown in **Figure 9(a)**, Yue [58] developed a safer alkaline leaching method - oxidation alkali leaching of the wastes to transform arsenic compounds into arsenate (AsO_4^{3-}) and subsequently recycling the alkali solution after arsenate removal, to treat the arsenic bearing wastes at a lower risk level.

There are a large number of reports that iron oxides have excellent adsorption and precipitation effects on heavy metal ions impurities in aqueous solutions, such as CrU and As. García-Sánchez et al. [59–60] found that goethite has a special adsorption effect and capacity for As ions. Wei Jiang [61] considers that arsenic [AsO_4^{3-}] absorbs on the surface of goethite by forming a bidentate-binuclear complex, and that pH and other metal ions in the solution will affect the distance and coordination number of As/Fe. His et al. [62] found that Uranyl can be adsorbed on goethite, amorphous ferric oxyhydroxide, and hematite sols at 25°C, and the adsorption effect on amorphous iron oxide is the strongest. Yue et al. [58] synthesized a series of high-concentrated ferric oxyhydroxide gels (HFGs) at different supersaturation to adsorb arsenate at high alkalinity, achieving zero-consume of the alkali resources. As is shown in **Figure 9(b)**, using HFG(I) that synthesized under the lowest super-saturation condition as the sorbent to treat the oxidation alkali leaching solution of the copper slag from real industry, the residual concentration of arsenic (As (V)) could decrease from 2084 to 71.8 mg/L, which fully meet the requirements for high-concentrated arsenic stabilization at high alkalinity and alkali resource recycling. To further improve the efficiency of filtration and separation, magnetic seed sowing and separation technology can also be introduced to make this process more complete. Related research is underway.

4.3 Removal of phosphate and starch in wastewater

Phosphorus and starch reportedly are the main wastewater contaminants that are difficult to remove efficiently [63–64]. When the phosphorus concentration in water exceeds 0.02 mg/L, phosphorus becomes a polluting element and causes eutrophication of water bodies [65–67]. Starch is a commonly used and cheap material, widely used in many chemical and material industries, but it produces high concentration of organic wastewater, which will affect the environment [68–70]. Therefore, phosphate and starch removal from wastewater has become the focus of many studies. The main phosphate and starch removal methods are similar, such as chemical precipitation [71–74], biological methods [75–79] and adsorption techniques [80–83]. Among them, Chemical precipitation and adsorption technology is commonly used in wastewater treatment due to the simple operation with low cost and large processing capacity compared to other methods [84–86]. However, chemical precipitation inevitably produces a large amount of fine precipitation and suspended solids, which seriously affect the sedimentation and filtration efficiency [84, 87]. And the adsorbents currently used in adsorption technology, such as activated carbon [70, 88], silica gel [89–90], membranes [91–93], etc., have

high production costs and poor adsorption performance, which greatly limits the adsorption effect and industrial applications.

Magnetic flocculation is an effective way to remove ultrafine suspended solids in water treatment [94–95]. It adds magnetic seeds to the aqueous solution to form magnetic flocs with the ultrafine suspended solids in the wastewater, and then passes through a magnetic separator to achieve rapid precipitation and separation [3, 95–96]. The combination of magnetic flocculation and chemical precipitation can make up for the shortcomings of ultrafine suspended solids and low separation efficiency of chemical precipitation. Magnetic flocculation has been widely used to treat wastewater with high pollution concentration [71], high turbidity [96] and high chemical oxygen demand (COD) [97]. It is worth noting that in many studies, iron-bearing minerals have shown the characteristics of removing phosphorus from aqueous solutions [98–99]. The iron-bearing minerals can be coordinated with phosphate and therefore have the potential to be used as adsorption materials for phosphorus and starch in wastewater [100–101].

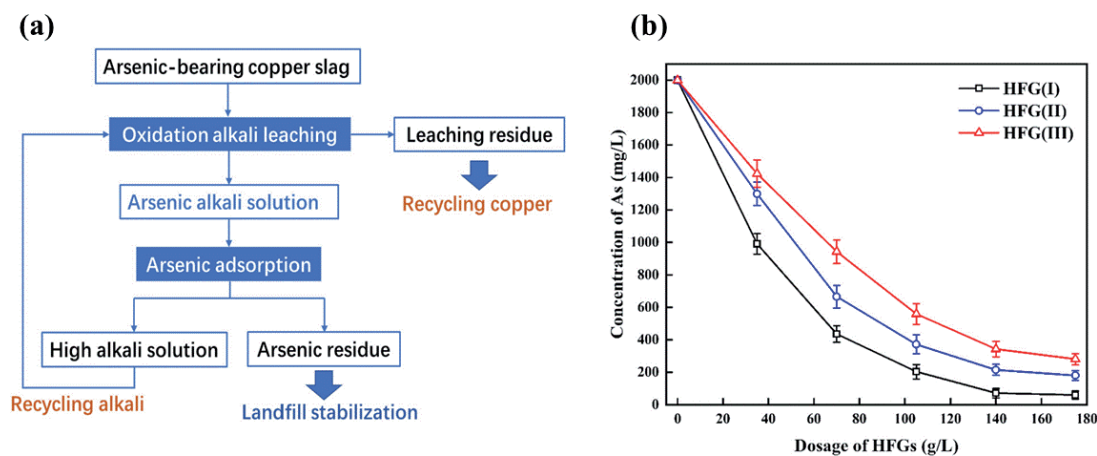


Figure 9.
(a) Flow diagram of the comprehensive treatment of the arsenic alkali residue and (b) arsenic removal from arsenic alkali solution with different HFG samples synthesized at pH 3(I), 7(II), and 11(III) [58].

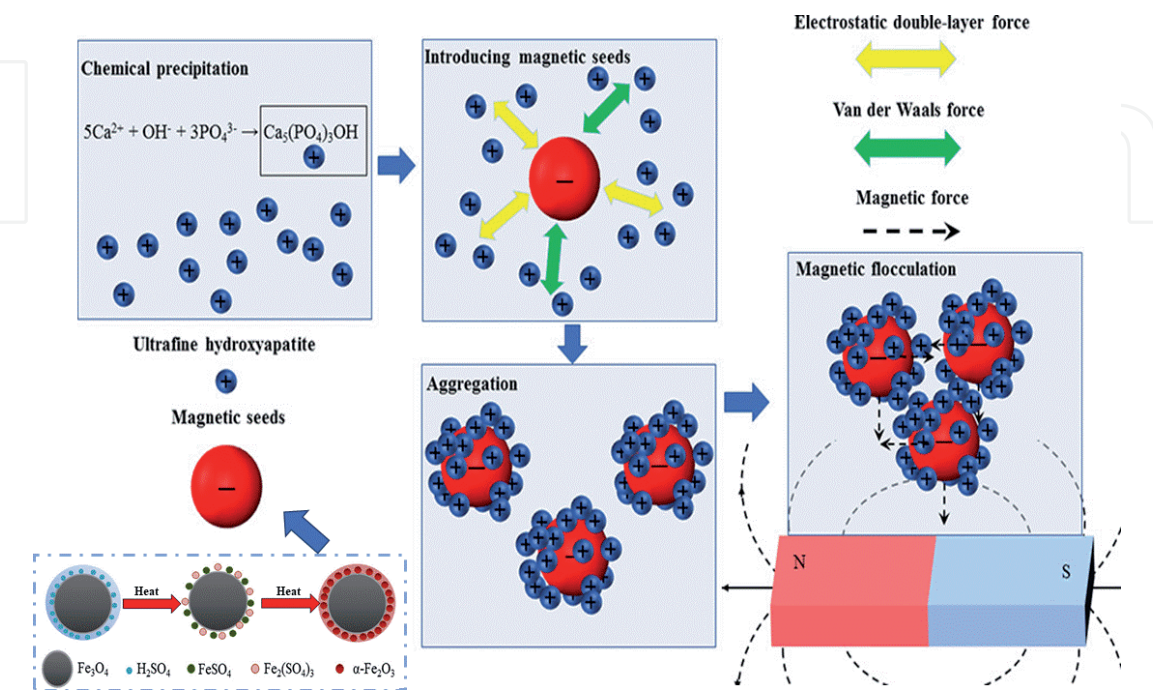


Figure 10.
The chemical precipitation and magnetic flocculation of removed hydroxyapatite contaminants [103].

Du et al. [102–103] combined the magnetic flocculation technology with iron-containing materials to prepare porous magnetic seeds with core-shell structure, which achieved simultaneous removal of starch and phosphate in wastewater. As shown in **Figure 10**, the core-shell magnetic seeds prepared by sulfation roasting of fine magnetite particles have a porous $\alpha\text{-Fe}_2\text{O}_3$ structure on the surface, and the specific surface area is three times larger [103–106]. As shown in **Figure 10**, the phosphate and starch in the wastewater can be adsorbed on magnetic seeds surface, and then separated from the wastewater by magnetic separation. The phosphorus and starch content in the wastewater are reduced to 1.51 and 9.51 mg/L, respectively, and the removal rate reaches more than 75% [102].

5. Conclusion

The iron removal method of the hydrometallurgical leachate is still dominated by the goethite process. The goethite process faces the disadvantages of high loss rate of valuable metals and difficulty in separation and filtration, which must be solved to get qualitative improvement. Careful adjustment of the pH value can help reduce metal loss, and inducing crystallization can increase the crystallinity of goethite and improve the separation and filtration efficiency. However, both methods can only focus on solving one of the problems and cannot reduce loss and promote filtration at the same time. The magnetite produced during the precipitation (crystallization) process opened a new path for magnetic separation, while the magnetite method is currently limited to laboratory research. In the present paper, the authors combined the goethite precipitation (crystallization) method with magnetic seed separation technology and developed a novel route. Goethite precipitates on the surface of the external magnetic seeds to form core-shell structured particles, which are efficiently separated by magnetic separation, and at the same time solve the two major problems of the traditional goethite process. This new method also shows advantages in the fields of arsenic and chromium removal from the leachate, phosphorus, and starch removal from wastewater and other fields. Goethite is the most common and stable crystalline iron oxide in soil and sediment. We expect that the goethite method combined with magnetic seed separation technology will show better results in the removal of organic dyeing, heavy metal ions, anions in wastewater and soil, and the adsorption and passivation of chemicals, nutrients, and harmful compounds in environments.

Acknowledgements

This work was supported by the Hunan Natural Science Foundation of China (No. 2020JJ5727), Innovation Driven Plan of Central South University (No. 2018CX036), National 111 Project (No. B14034), and Collaborative Innovation Center for Clean and Efficient Utilization of Strategic Metal Mineral Resources, Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources (No. 2018TP1002).

IntechOpen

Author details

Haisheng Han^{1,2*}, Wenjuan Sun^{1,2}, Wei Sun^{1,2} and Yuehua Hu^{1,2}

1 School of Minerals Processing and Bioengineering, Central South University, Changsha, China

2 Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, Central South University, Changsha, China

*Address all correspondence to: hanhai5086@csu.edu.cn

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Wu Y, Tan D, Ding W, Guo S. Goethite process for removing of iron in hydrometallurgy. *Hydrometallurgy*. 2014;**000**(002):86-89
- [2] Loan M, Newman OMG, Copper RMG, et al. Defining the paragoethite process for iron removal in zinc hydrometallurgy. *Hydrometallurgy*. 2006;**81**(2):104-129. DOI: 10.1016/j.hydromet.2005.11.002
- [3] Han H, Sun W, Hu Y, et al. Magnetite precipitation for iron removal from nickel-rich solutions in hydrometallurgy process. *Hydrometallurgy*. 2016;**165**: 318-322. DOI: 10.1016/j.hydromet.2016.01.006
- [4] McDonald RG, Whittington BL. Atmospheric acid leaching of nickel laterites review. Part I. Sulphuric acid technologies. *Hydrometallurgy*. 2008;**91**(1-4):35-55. DOI: 10.1016/j.hydromet.2007.11.009
- [5] Claassen JO, Meyer EHO, Rennie J, et al. Iron precipitation from zinc-rich solutions: Defining the Zincor process. *Hydrometallurgy*. 2002;**67**(1-3):87-108. DOI: 10.1016/S0304-386X(02)00141-X
- [6] Swarnkar SR, Gupta BL, Dhana Sekharan R. Iron control in zinc plant residue leach solution. *Hydrometallurgy*. 1996;**42**(1):21-26. DOI: 10.1016/0304-386X(95)00077-T
- [7] Ismael MRC, Carvalho JMR. Iron recovery from sulphate leach liquors in zinc hydrometallurgy. *Minerals Engineering*. 2003;**16**(1):31-39. DOI: 10.1016/S0892-6875(02)00310-2
- [8] Dutrizac J. An overview of iron precipitation in hydrometallurgy. In: Strathdee GL, Klein MO, Melis LA, editors. *Crystallization and Precipitation*. 2nd ed. Pergamon Press; 1987. p. 259-283. DOI: 10.1016/B978-0-08-035751-5.50038-6
- [9] Davey PT, Scott TR. Removal of iron from leach liquors by the "goethite" process. *Hydrometallurgy*. 1976;**2**(1):25-33. DOI: 10.1016/0304-386X(76)90011-6
- [10] Pradel J, Castillo S, Traverse JP, et al. Ferric hydroxide oxide from the goethite process: Characterization and potential use. *Industrial and Engineering Chemistry Research*. 1993;**32**(9):1801-1804. DOI: 10.1021/ie00021a001
- [11] Allan R, Haigh C, Hamdorf J. Method of Removing Dissolved Ferric Iron from Iron-Bearing Solutions. U.S. Patent 3781405DA.1973-12-25
- [12] Han H, Sun W, Hu Y, et al. The application of zinc calcine as a neutralizing agent for the goethite process in zinc hydrometallurgy. *Hydrometallurgy*. 2014;**147-148**: 120-126. DOI: 10.1016/j.hydromet.2014.05.005
- [13] Schlechtriem C, Ricci M, Focken U, et al. On a new method of removing iron from saline solutions as in the alum or sulphate of alumina manufactures from baunite, or other aluminous minerals. *Journal of Chemical Technology & Biotechnology*. 2010;**1**(7):275-285. DOI: 10.1002/jctb.5000010704
- [14] Pelino M, Cantalini C, Abbruzzese C, et al. Treatment and recycling of goethite waste arising from the hydrometallurgy of zinc. *Hydrometallurgy*. 1995;**40**(1-2):25-35. DOI: 10.1016/0304-386X(95)00004-Z
- [15] Reddy DHK, Yun YS. Spinel ferrite magnetic adsorbents: Alternative future materials for water purification? *Coordination Chemistry Reviews*. 2016;**315**:90-111. DOI: 10.1016/j.ccr.2016.01.012
- [16] Reiss G, Hütten A. Magnetic nanoparticles: Applications beyond

- data storage. *Nature Materials*. 2005;**4**(10):725-726. DOI: 10.1038/nmat1494
- [17] Hokkanen S, Repo E, Lou S, et al. Removal of arsenic(V) by magnetic nanoparticle activated microfibrillated cellulose. *Chemical Engineering Journal*. 2015;**260**:886-894
- [18] Ying A, Hou H, Liu S, et al. Ionic modified TBD supported on magnetic nanoparticles: A highly efficient and recoverable catalyst for organic transformations. *ACS Sustainable Chemistry & Engineering*. 2016;**4**(2):625-632. DOI: 10.1021/acssuschemeng.5b01757
- [19] Tabakova T, Andreeva D, Andreev A, et al. Mechanism of the oxidative hydrolysis of iron(II) sulphate. *Journal of Materials Science: Materials in Electronics*. 1992;**3**(4):201-205. DOI: 10.1007/BF00703026
- [20] Andreeva D, Mitov I, Tabakova T, et al. Formation of goethite by oxidative hydrolysis of iron(II) sulphate. *Journal of Materials Science: Materials in Electronics*. 1994;**5**(3):168-172. DOI: 10.1007/BF01198949
- [21] Babcan J. Synthesis of jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. *Geology*. 1971;**22**(2):299-304
- [22] Claassen JO, Sandenbergh RF. Influence of mixing on the quality of iron precipitates in zinc-rich solutions. *Hydrometallurgy*. 2007;**87**(3-4):112-123. DOI: 10.1016/j.hydromet.2007.02.002
- [23] Yue T, Han H, Sun W, et al. Low-pH mediated goethite precipitation and nickel loss in nickel hydrometallurgy. *Hydrometallurgy*. 2016;**165**:238-243. DOI: 10.1016/j.hydromet.2016.03.004
- [24] Chang Y, Zhai X, Li B, et al. Removal of iron from acidic leach liquor of lateritic nickel ore by goethite precipitate. *Hydrometallurgy*. 2010;**101**(1-2):84-87. DOI: 10.1016/j.hydromet.2009.11.014
- [25] Han H, Sun W, Hu Y, et al. Magnetic separation of iron precipitate from nickel sulfate solution by magnetic seeding. *Hydrometallurgy*. 2015;**156**:182-187. DOI: 10.1016/j.hydromet.2015.07.001
- [26] Kamimura Y, Lyoki K, Elangovan S, et al. OSDA-free synthesis of MTW-type zeolite from sodium aluminosilicate gels with zeolite beta seeds. *Microporous and Mesoporous Materials*. 2012;**163**:282-290. DOI: 10.1016/j.micromeso.2012.07.014
- [27] Ran Z, Sun Y, Chang B, et al. Silica composite nanoparticles containing fluorescent solid core and mesoporous shell with different thickness as drug carrier. *Journal of Colloid and Interface Science*. 2013;**410**:94-101. DOI: 10.1016/j.jcis.2013.08.015
- [28] Murphy CJ, Thompson LB, Chernak DJ, et al. Gold nanorod crystal growth: From seed-mediated synthesis to nanoscale sculpting. *Current Opinion in Colloid & Interface Science*. 2011;**16**(2):128-134. DOI: 10.1016/j.cocis.2011.01.001
- [29] Wu Y, Ren X, Lu Y, et al. Crystallization and morphology of zeolite MCM-22 influenced by various conditions in the static hydrothermal synthesis. *Microporous and Mesoporous Materials*. 2008;**112**(1-3):138-146. DOI: 10.1016/j.micromeso.2007.09.022
- [30] Han H, Sun W, Hu Y, et al. Induced crystallization of goethite precipitate from nickel sulfate solution by limonite seeding. *Hydrometallurgy*. 2017;**174**:253-257. DOI: 10.1016/j.hydromet.2017.03.001
- [31] Yue T, Xu Z, Hu Y, et al. Magnetic separation and recycling of goethite and calcium sulfate in zinc hydrometallurgy in the presence of maghemite fine

- particles. *ACS Sustainable Chemistry & Engineering*. 2018;**6**(2):1532-1538. DOI: 10.1021/acssuschemeng.7b03856
- [32] Yue T, Sun W, Hu Y, et al. Mechanism of goethite precipitation on magnetite and maghemite nanoparticles studied by surface complexation/precipitation modeling. *Langmuir*. 2018;**34**(50):15134-15142. DOI: 10.1021/acs.langmuir.8b02571
- [33] Cao S, Wang K, Zhou S, et al. Mechanism and effect of high-basicity chromium agent acting on Cr-wastewater-reuse system of leather industry. *ACS Sustainable Chemistry & Engineering*. 2018;**6**(3):3957-3963. DOI: 10.1021/acssuschemeng.7b04282
- [34] Chrysochoou M, Dermatas D. Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: Literature review and experimental study. *Journal of Hazardous Materials*. 2006;**136**(1):20-33. DOI: 10.1016/j.jhazmat.2005.11.008
- [35] De Souza E, Silva PT, De Mello NT, et al. Extraction and recovery of chromium from electroplating sludge. *Journal of Hazardous Materials*. 2006;**128**(1):39-43. DOI: 10.1016/j.jhazmat.2005.07.026
- [36] Lin WY, Heng KS, Sun XL, et al. Influence of moisture content and temperature on degree of carbonation and the effect on Cu and Cr leaching from incineration bottom ash. *Waste Management*. 2015;**43**:264-272. DOI: 10.1016/j.wasman.2015.05.029
- [37] Magalhães JM, Sliva JE, Castro FP, et al. Role of the mixing conditions and composition of galvanic sludges on the inertization process in clay-based ceramics. *Journal of Hazardous Materials*. 2004;**106**(2-3):169-176. DOI: 10.1016/j.jhazmat.2003.11.011
- [38] Qian G, Yang X, Dong S, et al. Stabilization of chromium-bearing electroplating sludge with MSWI fly ash-based Friedel matrices. *Journal of Hazardous Materials*. 2009;**165**(1-3):955-960. DOI: 10.1016/j.jhazmat.2008.10.078
- [39] Adhoum N, Monster L, Bellakhal N, et al. Treatment of electroplating wastewater containing Cu^{2+} , Zn^{2+} and Cr(VI) by electrocoagulation. *Journal of Hazardous Materials*. 2004;**112**(3):207-213. DOI: 10.1016/j.jhazmat.2004.04.018
- [40] Kul M, Oskay KO. Separation and recovery of valuable metals from real mix electroplating wastewater by solvent extraction. *Hydrometallurgy*. 2015;**155**:153-160
- [41] Hu J, Chen G, Lo IMC. Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. *Water Research*. 2005;**39**(18):4528-4536. DOI: 10.1016/j.watres.2015.04.021
- [42] Miretzky P, Cirelli AF. Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review. *Journal of Hazardous Materials*. 2010;**180**(1-3):1-19. DOI: 10.1016/j.jhazmat.2010.04.060
- [43] Suksabye P, Thiravetyan P. Cr(VI) adsorption from electroplating wastewater by chemically modified coir pith. *Journal of Environmental Management*. 2012;**102**:1-8. DOI: 10.1016/j.jenvman.2011.10.020
- [44] Wen T, Wang J, Yu S, et al. Magnetic porous carbonaceous material produced from tea waste for efficient removal of As(V) , Cr(VI) , humic acid, and dyes. *ACS Sustainable Chemistry & Engineering*. 2017;**5**(5):4371-4380. DOI: 10.1021/acssuschemeng.7b00418
- [45] Aoki T, Munemori M. Recovery of chromium(VI) from wastewaters with iron(III) hydroxide-I adsorption mechanism of chromium(VI) on iron(III) hydroxide. *Water*

Research. 1982;**16**(6):793-796. DOI: 10.1016/0043-1354(82)90006-9

[46] Erdem M, Tumen F. Chromium removal from aqueous solution by the ferrite process. *Journal of Hazardous Materials*. 2004;**109**(1-3):71-77. DOI: 10.1016/j.jhazmat.2004.02.031

[47] Sass BM, Rai D. Solubility of amorphous chromium(III)-iron(III) hydroxide solid solutions. *Inorganic Chemistry*. 1987;**26**(14):2228-2232. DOI: 10.1002/chin.198743013

[48] Ye Y, Jiang Z, et al. Efficient removal of Cr(III)-organic complexes from water using UV/Fe(III) system: Negligible Cr(VI) accumulation and mechanism. *Water Research*. 2017;**126**:172-178. DOI: 10.1016/j.watres.2017.09.021

[49] Yue T, Niu Z, Hu Y, et al. Cr(III) and Fe(II) recovery from the polymetallic leach solution of electroplating sludge by Cr(III)-Fe(III) coprecipitation on maghemite. *Hydrometallurgy*. 2019;**184**:132-139. DOI: 10.1016/j.hydromet.2018.11.013

[50] Nidheesh PV, Singh TSA. Arsenic removal by electrocoagulation process: Recent trends and removal mechanism. *Chemosphere*. 2017;**181**:418-432. DOI: 10.1016/j.chemosphere.2017.04.082

[51] Luong VT, Cañas Kurz EE, Hellriegel U, et al. Iron-based subsurface arsenic removal technologies by aeration: A review of the current state and future prospects. *Water Research*. 2018;**133**:110-122. DOI: 10.1016/j.watres.2018.01.007

[52] Morales NA, Martínez D, García-Meza JV, et al. Total and bioaccessible arsenic and lead in soils impacted by mining exploitation of Fe-oxide-rich ore deposit at Cerro de Mercado, Durango, Mexico. *Environment and Earth Science*. 2015;**73**(7):3249-3261. DOI: 10.1007/s12665-014-3617-7

[53] Xiong Y, Tong Q, Shan W, et al. Arsenic transformation and adsorption by iron hydroxide/manganese dioxide doped straw activated carbon. *Applied Surface Science*. 2017;**416**:618-627. DOI: 10.1016/j.apsusc.2017.04.145

[54] Mohan D, Pittman CU. Arsenic removal from water/wastewater using adsorbents-A critical review. *Journal of Hazardous Materials*. 2007;**142**(1-2):1-53. DOI: 10.1016/j.jhazmat.2007.01.006

[55] Luo T, Cui J, Hu S, et al. Arsenic removal and recovery from copper smelting wastewater using TiO₂. *Environmental Science & Technology*. 2010;**44**(23):9094-9098. DOI: 10.1021/es1024355

[56] Basha CA, Somasundaram M, Kannadasan T, et al. Heavy metals removal from copper smelting effluent using electrochemical filter press cells. *Chemical Engineering Journal*. 2011;**171**(2):563-571. DOI: 10.1016/j.cej.2011.04.031

[57] Ke Y, Shen C, Min XB, et al. Separation of Cu and As in Cu-As-containing filter cakes by Cu²⁺-assisted acid leaching. *Hydrometallurgy*. 2017;**172**:45-50. DOI: 10.1016/j.hydromet.2017.06.022

[58] Yue T, Niu Z, Hu Y, et al. Arsenic(V) adsorption on ferric oxyhydroxide gel at high alkalinity for securely recycling of arsenic-bearing copper slag. *Applied Surface Science*. 2019;**478**:213-220. DOI: 10.1016/j.apsusc.2019.01.249

[59] García-Sánchez A, Alastuey A, Querol X. Heavy metal adsorption by different minerals: Application to the remediation of polluted soils. *Science of the Total Environment*. 1999;**242**(1):179-188. DOI: 10.1016/S0048-9697(99)00383-6

[60] Donat R. The removal of uranium (VI) from aqueous solutions onto natural sepiolite. *The Journal*

of Chemical Thermodynamics. 2009;**41**(7):829-835. DOI: 10.1016/j.jct.2009.01.009

[61] Jiang W, Lv J, Luo L, et al. Arsenate and cadmium co-adsorption and co-precipitation on goethite. *Journal of Hazardous Materials*. 2013;**262**:55-63. DOI: 10.1016/j.jhazmat.2013.08.030

[62] His CKD, Langmuir D. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica et Cosmochimica Acta*. 1985;**49**(9):1931-1941. DOI: 10.1016/0016-7037(85)90088-2

[63] Jeon KJ, Ahn JH. Evaluation of titanium tetrachloride and polytitanium tetrachloride to remove phosphorus from wastewater. *Separation and Purification Technology*. 2018;**197**:197-201. DOI: 10.1016/j.seppur.2018.01.016

[64] Lin CY, Nguyen MLT, Lay CH. Starch-containing textile wastewater treatment for biogas and microalgae biomass production. *Journal of Cleaner Production*. 2017;**168**:331-337. DOI: 10.1016/j.jclepro.2017.09.036

[65] Ménesguen A, Lacroix G. Modelling the marine eutrophication: A review. *Science of the Total Environment*. 2018;**636**:339-354. DOI: 10.1016/j.scitotenv.2018.04.183

[66] USEP Agency. Nutrient Criteria Technical Guidance Manual: Rivers and Streams. Washington: EPA; 2000

[67] Liu F, Yang J, Zuo J, et al. Graphene-supported nanoscale zero-valent iron: Removal of phosphorus from aqueous solution and mechanistic study. *Journal of Environmental Sciences (China)*. 2014;**26**(8):1751-1762. DOI: 10.1016/j.jes.2014.06.016

[68] Guo J, Zhang Y, Zhao J, et al. Characterization of a bioflocculant from potato starch wastewater and

its application in sludge dewatering. *Applied Microbiology and Biotechnology*. 2015;**99**(13):5429-5437. DOI: 10.1007/s00253-015-6567-4

[69] Vera L, Sun W, Iftikhar M, et al. LCA based comparative study of a microbial oil production starch wastewater treatment plant and its improvements with the combination of CHP system in Shandong, China. *Resources, Conservation & Recycling*. 2015;**96**:1-10. DOI: 10.1016/j.resconrec.2014.09.013

[70] Khlestkin VK, Peltek SE, Kolchanov NA. Review of direct chemical and biochemical transformations of starch. *Carbohydrate Polymers*. 2018;**181**:460-476. DOI: 10.1016/j.carbpol.2017.10.035

[71] Cichy B, Kuźdzał E, Krztoń H. Phosphorus recovery from acidic wastewater by hydroxyapatite precipitation. *Journal of Environmental Management*. 2019;**232**:421-427. DOI: 10.1016/j.jenvman.2018.11.072

[72] Johnston AE, Richards IR. Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use and Management*. 2003;**19**(1):45-49. DOI: 10.1079/SUM2002162

[73] Chang Y, Yan X, Wang Q, et al. High efficiency and low cost preparation of size controlled starch nanoparticles through ultrasonic treatment and precipitation. *Food Chemistry*. 2017;**227**:369-375. DOI: 10.1016/j.foodchem.2017.01.111

[74] dos Santos JD, Veit MT, Juchen PT, et al. Use of different coagulants for cassava processing wastewater treatment. *Journal of Environmental Chemical Engineering*. 2018;**6**(2):1821-1827. DOI: 10.1016/j.jece.2018.02.039

[75] Verstraete W, Van de Caveye P, Diamantis V. Maximum use of

resources present in domestic “used water”. *Bioresource Technology*. 2009;**100**(23):5537-5545. DOI: 10.1016/j.biortech.2009.05.047

[76] Liu YN, Xue G, Yu SI. Comparing results of cultured and uncultured biological methods used in biological phosphorus removal. *Journal of Environmental Sciences*. 2007;**19**(11):1373-1379. DOI: 10.1016/S1001-0742(07)60224-1

[77] Luo D, Yuan L, Liu L, et al. The mechanism of biological phosphorus removal under anoxic-aerobic alternation condition with starch as sole carbon source and its biochemical pathway. *Biochemical Engineering Journal*. 2018;**132**:90-99. DOI: 10.1016/j.bej.2018.01.007

[78] Wang RM, Wang Y, Ma GP, et al. Efficiency of porous burnt-coke carrier on treatment of potato starch wastewater with an anaerobic-aerobic bioreactor. *Chemical Engineering Journal*. 2009;**148**(1):35-40. DOI: 10.1016/j.cej.2008.07.028

[79] Zou H, Wang Y. Phosphorus removal and recovery from domestic wastewater in a novel process of enhanced biological phosphorus removal coupled with crystallization. *Bioresource Technology*. 2016;**211**:87-92. DOI: 10.1016/j.biortech.2016.03.073

[80] Nie G, Wu L, Du Y, et al. Efficient removal of phosphate by a millimeter-sized nanocomposite of titanium oxides encapsulated in positively charged polymer. *Chemical Engineering Journal*. 2019;**360**:1128-1136. DOI: 10.1016/j.cej.2018.10.184

[81] Chen L, Li Y, Sun Y, et al. La(OH)₃ loaded magnetic mesoporous nanospheres with highly efficient phosphate removal properties and superior pH stability. *Chemical Engineering Journal*. 2019;**360**:342-348. DOI: 10.1016/j.cej.2018.11.234

[82] Lü C, Yan D, He J, et al. Environmental geochemistry significance of organic phosphorus: An insight from its adsorption on iron oxides. *Applied Geochemistry*. 2017;**84**:52-60. DOI: 10.1016/j.apgeochem.2017.05.026

[83] Zhang X, Lin X, He Y, et al. Adsorption of phosphorus from slaughterhouse wastewater by carboxymethyl konjac glucomannan loaded with lanthanum. *International Journal of Biological Macromolecules*. 2018;**119**:105-115. DOI: 10.1016/j.ijbiomac.2018.07.140

[84] Ye Y, Ngo HH, Guo W, et al. Insight into chemical phosphate recovery from municipal wastewater. *The Science of the Total Environment*. 2017;**576**:159-171. DOI: 10.1016/j.scitotenv.2016.10.078

[85] De-Bashan LE, Bashan Y. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research*. 2004;**38**(19):4222-4246. DOI: 10.1016/j.watres.2004.07.014

[86] Parsons SA, Smith JA. Phosphorus removal and recovery from municipal wastewaters. *Elements*. 2008;**4**(2):109-112. DOI: 10.2113/GSELEMENTS.4.2.109

[87] Pratt C, Parsons SA, Soares A, et al. Biologically and chemically mediated adsorption and precipitation of phosphorus from wastewater. *Current Opinion in Biotechnology*. 2012;**23**(6):890-896. DOI: 10.1016/j.copbio.2012.07.003

[88] Novais RM, Caetano APF, Seabra MP, et al. Extremely fast and efficient methylene blue adsorption using eco-friendly cork and paper waste-based activated carbon adsorbents. *Journal of Cleaner Production*. 2018;**197**:1137-1147. DOI: 10.1016/j.jclepro.2018.06.278

- [89] Choi JM, Jeong D, Cho E, et al. Chemically functionalized silica gel with alkynyl terminated monolayers as an efficient new material for removal of mercury ions from water. *Journal of Industrial and Engineering Chemistry*. 2016;**35**:376-382. DOI: 10.1016/j.jiec.2016.01.020
- [90] Salama A, Aljohani HA, Shoueir KR. Oxidized cellulose reinforced silica gel: New hybrid for dye adsorption. *Materials Letters*. 2018;**230**:293-296. DOI: 10.1016/j.matlet.2018.07.131
- [91] Damtie MM, Kim B, Woo YC, et al. Membrane distillation for industrial wastewater treatment: Studying the effects of membrane parameters on the wetting performance. *Chemosphere*. 2018;**206**:793-801. DOI: 10.1016/j.chemosphere.2018.05.070
- [92] Lv Y, Yan H, Yang B, et al. Bipolar membrane electrodialysis for the recycling of ammonium chloride wastewater: Membrane selection and process optimization. *Chemical Engineering Research and Design*. 2018;**138**:105-115. DOI: 10.1016/j.cherd.2018.08.014
- [93] Zhang Y, Wei S, Hu Y, et al. Membrane technology in wastewater treatment enhanced by functional nanomaterials. *Journal of Cleaner Production*. 2018;**197**:339-348. DOI: 10.1016/j.jclepro.2018.06.211
- [94] Yeap SP, Tia SY. Induced rapid magnetic sedimentation of stabilized-Fe₃O₄ nanoparticles by bridging and depletion flocculation. *Chemical Engineering Research and Design*. 2019;**142**:53-61. DOI: 10.1016/j.cherd.2018.12.004
- [95] Tang H, Wang L, Sun W, et al. Electric arc furnace dust as magnetic carrier particles for removal of micro-fine particles from suspensions. *Separation and Purification Technology*. 2017;**176**:220-230. DOI: 10.1016/j.seppur.2016.12.024
- [96] Lv M, Zhang Z, Zeng J, et al. Roles of magnetic particles in magnetic seeding coagulation-flocculation process for surface water treatment. *Separation and Purification Technology*. 2019;**212**:337-343. DOI: 10.1016/j.seppur.2018.11.011
- [97] Ren W, Zhou Z, Jiang LM, et al. A cost-effective method for the treatment of reject water from sludge dewatering process using supernatant from sludge lime stabilization. *Separation and Purification Technology*. 2015;**142**:123-128. DOI: 10.1016/j.seppur.2014.12.037
- [98] Li B, Ma W, Wang H, et al. Optimization study on polymeric ferric sulfate (PFS) phosphorous depth removal. *Applied Mechanics and Materials*. 2011;**71-78**:3219-3223. DOI: 10.4028/www.scientific.net/AMM.71-78.3219
- [99] Ruihua L, Lin Z, Tao T, et al. Phosphorus removal performance of acid mine drainage from wastewater. *Journal of Hazardous Materials*. 2011;**190**(1-3):669-676. DOI: 10.1016/j.jhazmat.2011.03.097
- [100] Yan J, Jiang T, Yao T, et al. Preliminary investigation of phosphorus adsorption onto two types of iron oxide-organic matter complexes. *Journal of Environmental Sciences (China)*. 2016;**42**:152-162. DOI: 10.1016/j.jes.2015.08.008
- [101] Yang X, He J, Sun Z, et al. Effect of phosphate on heterogeneous Fenton oxidation of catechol by nano-Fe₃O₄: Inhibitor or stabilizer? *Journal of Environmental Sciences (China)*. 2016;**39**:69-76. DOI: 10.1016/j.jes.2015.11.007
- [102] Du C, Hu Y, Han H, et al. Magnetic separation of phosphate contaminants from starch wastewater using magnetic

seeding. *The Science of the Total Environment*. 2019;**695**:133723. DOI: 10.1016/j.scitotenv.2019.133723

[103] Du C, Yu J, Sun W, et al. Purification of starch and phosphorus wastewater using core-shell magnetic seeds prepared by sulfated roasting. *Journal of Environmental Sciences (China)*. 2019;**81**:4-16. DOI: 10.1016/j.jes.2019.02.014

[104] Hemmelmann JC, Xu H, Krumm W. Empirical modeling of iron oxide dissolution in sulphuric and hydrochloric acid. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*. 2013;**44**(5):1232-1235. DOI: 10.1007/s11663-013-9893-x

[105] Huang P, Deng S, Zhang Z, et al. A sustainable process to utilize ferrous sulfate waste from titanium oxide industry by reductive decomposition reaction with pyrite. *Thermochimica Acta*. 2015;**620**:18-27. DOI: 10.1016/j.tca.2015.10.004

[106] Ponomar VP, Dudchenko NO, Brik AB. Reduction roasting of hematite to magnetite using carbohydrates. *International Journal of Mineral Processing*. 2017;**164**:21-25. DOI: 10.1016/j.minpro.2017.05.005