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Application of waste iron in ferrate(VI) synthesis and phenol removal as confirmation of efficiency

Ljiljana Nikolić Bujanović[1, *], Milan Čekerevac[2], Miloš Simičić[2], Milena Tomić[2]

[1]Faculty of Ecology and Environmental Protection, University Union-Nikola Tesla, Belgrade, Serbia
[2]IHIS Techno-experts, Research and Development Center, Batajnički put 23, Belgrade, Serbia

[*]**Corresponding author:** ljnikolicbujanovic@unionnikolatesla.edu.rs, bujanovic08@gmail.com

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Abstract: Ferrate (VI) is a strong oxidizing, coagulating and flocculating agent. Due to its characteristics, it is suitable for treatment of waters of different origins. In these processes, resulting is an environmentally friendly and non-toxic product, $Fe(OH)_3$, which according to the results of this paper can be recycled and re-synthesized to ferrate(VI). This paper presents a method for the synthesis of ferrate salts by oxidation process from steel pickling wastewater containing $FeCl_2$ and $FeCl_3$ salts. The method for synthesis involves the process of oxidation of ferrous and ferric ions by means of $Ca(ClO)_2$ in solid state and in the presence of KOH in solid state. The recording of the x-ray diffractometer demonstrates a significant presence of K_2FeO_4, while analysis revealed a yield of 15%.

The application of ferrate synthesized from waste iron is shown in the process of treating waste water from the wood industry. The example given of this paper is treatment of samples of WW from the wood industry, from the thermal dryer and steam chamber, using the Jar procedure. The initial concentration of phenol in the sample from the thermal dryer was 27 mg/l and in the sample from the steam chamber 30 mg/l. This wastewater also has a high content of natural organic matter (COD of the sample from the thermal dryer was 3233.1 mgO2/l and COD of the sample from the steam chamber was 4692.1 mgO2/l). The efficiency of removal of phenol by ferrate(VI) was 74.85% and 72.67% for samples from the thermal dryer and the steam chamber, respectively.

Keywords: potassium ferrate, ferrous chloride, ferric chloride, phenol, x-ray

1. Introduction

Ferrate(VI) salts have a wide range of potential applications due to their high efficient oxidation performance. In the area of environmental application ferrate has been considered for water and wastewater treatment because of its environmentally friendly properties without hazardous compounds forming, such as chlorine or bromine, carcinogenic organic pollutants (Audette et al., 1971; J. Q. Jiang & Lloyd, 2002; Yunho et al., 2004). Due to the fact that Fe(III), generated during oxidation by ferrate, exhibits valuable coagulating properties makes an additional contribution to water treatment processes.

Research works performed by Fremy(Fremy, 1841, 1842)are frequently cited in literature as the first to scientifically reveal the existence of iron in a hexavalent state and to effectively achieve ferrates synthesis. Since then, the preparation methods, developed mostly on a laboratory scale, have made little progress, and can be classified into three groups:

- The high temperature route consisting of heating and/or melting various iron oxides bearing materials under high concentration of alkali substances and oxygen flow (Kiselev et al., 1989). These synthesis methods, performed at temperatures as high as 800°C, seem to be mostly ineffective since Fe(VI) is not stable at temperatures higher than 200°C. Most probably, Fe(VI) resulted from the dismutation of synthetized Fe(IV) and/or Fe(V) during manipulation of the synthesis product.
- The wet/humid oxidation of Fe(III) salts bearing solutions, under strong alkaline conditions, using hypochlorite or chlorine as an oxidant. This method is the most used since the 1950s (Ockerman & Schreyer, 1951; Schreyer et al., 1953). One of the drawbacks is that the wet

method used pure chemicals and required many operations for Fe(VI) preparation and separation, making it very costly. Moreover, the water reacts with ferrate leading to its reduction into Fe(III).

- The electrochemical method (Licht et al., 2002; Mácová et al., 2009; L. N. Nikolić-Bujanović et al., 2012), by anodic dissolution of iron or its alloys in a strong alkaline solution (pH > 10) in the transpassive region. Ferrate obtained by electrochemical synthesis has many advantages compared to chemically synthesized ferrate (Mácová et al., 2009), such as: simplicity, lower consumption of chemicals, non-toxic products and exceptional purity of obtained ferrate. However, the decomposition of Fe(VI) by water, low current efficiency and anode passivation are some of the concerns for this route.

Ferrate(VI) salt is a potent oxidant. Under acidic and alkaline conditions, its respective reduction potentials are 2.20 and 0.700 V, being a potential for replacing traditional oxidants, such as ozone, hypochlorite, permanganate, and others(Audette et al., 1971); their respective half-cell reduction potentials in acidic conditions are 2.08, 1.48, and 1.69 V, respectively (Yunho et al., 2004), all less than Fe(VI). Potassium ferrate, other than acting as a powerful oxidant, can be an inorganic coagulant when chemically reduced to $Fe(OH)_3$; it can effectively remove suspended solids, heavy metals, and a variety of contaminants from water (J. Q. Jiang & Lloyd, 2002). Further, using traditional oxidants to treat pollutants/contaminants usually can result in a noteworthy toxic byproduct problem, such as tri-halo-methane and bromates (Gombos et al., 2012). In contrast, potassium ferrate, as a water treatment agent, is reduced to environment friendly $Fe(OH)_3$ (J. Q. Jiang & Lloyd, 2002). Prior to the chlorination process for drinking water, using Fe(VI) as a pre-treatment agent can effectively reduce the formation of hazardous by-products (Yang et al., 2013).

Despite the advantages Fe(VI) can provide, it is expensive for using it to treat pollutants and contaminants. There is also the problem of removing the resulting $Fe(OH)_3$ precipitate which also contains the removed pollutants. The paper presents the possibility of recycling $Fe(OH)_3$ from which Fe(VI) is recovered by a chemical process. For example, synthesizing Fe(VI) by using spent steel pickling liquid as an iron source can achieve a dual-win benefit by not only reducing the cost of Fe - raw chemicals source for Fe(VI) synthesis but also recycling spent steel pickling liquid for environmental sustainability.

Spent pickling liquid is unwantedly produced by the steel industry. Products like steel plates, pipes, and coils always require cleaning with acid to remove their surface impurities before being subjected to further processing. The impurities include black surfaces, iron oxides, and other contaminants. Hydrochloric acid is usually used as the pickling acid for carbon steel products due to its relatively lower price, lower acid consumption rate, and providing a faster pickling process, despite its shortcomings of a higher volatilization rate (Agrawal & Sahu, 2009).

If spent pickling liquid is treated as waste water, toxic metal present in it is generally removed through different approaches, such as the precipitation method, ion exchange, and others. Among them, precipitation as hydroxide is the most often used technology. Although the technology is technically simple, its neutralization step requires a large amount of alkaline or alkaline earth-based chemicals, and it would be much more praised if spent steel pickling liquid could be recycled.

When hydrochloric acid is used as a pickling agent, most iron in spent steel pickling liquid would be present in the form of ferrous chloride through the following chemical reaction (Agrawal & Sahu, 2009)

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O \qquad (1)$$

A large amount of attention has recently been focused on the removal of phenol and its derivatives from wastewater (WW) due to their toxicity and high concentration in wastewater. Phenol is a common pollutant in industrial discharges and is also believed to be an intermediate product in the oxidation process of higher molecular weight aromatic hydrocarbons. Their high concentration in the WW of wood industry originates from pentachlorophenol (PCP), which is used for wood conservation (Lee et al., 1991).

The contamination of water system by phenols and their compounds is a major problem because of the toxicity of phenol even at low concentrations. Toxic phenol concentrations are in the range of 10 - 24 mg / l for humans and from 9 - 25 mg / l for aquatic life. Lethal concentration of phenol is around 150mg / 100ml. Phenol and phenolic compounds are designated as priority pollutants by the Environmental Protection Agency in the US, and take 11th place in the list of 126 undesirable chemicals (Environmental Protection Agency). (Environmental Protection Agency (EPA), Manual Report for List of Chemical Priority, USA, (2002)).

Phenol and phenolic compounds are classified as teratogenic and carcinogenic compounds (Iurascu et al., 2009). Phenolic compounds are well known for high salinity, acidity, chemical oxygen demand (COD) and low biodegradability (Turhan & Uzman, 2008). In addition, they have low volatilities and easily form azeotropes and eutectics(López-Montilla et al., 2005). All these properties make them difficult to treat.

Phenol has acute and chronic effects on human health. Inhalation and dermal exposure to phenol is highly irritating to skin, eyes, and mucous. The other acute health effects are headache, dizziness, fatigue, fainting, weakness, nausea, vomiting and lack of appetite at high levels. Effects from chronic exposure (longer than 365 days) include irritation of the gastrointestinal tract. Phenol also can change blood pressure and can cause liver and kidney damage. Nervous system is affected negatively for long time exposures (EPA, 2002). Animal studies have not shown tumors resulting from oral exposure to phenol, while dermal studies have reported that phenol applied to the skin may be a tumor promotor and/or a weak skin carcinogen in mice.

Due to its toxicity to aquatic life and humans, regulations for phenol concentration in WW are very strict. Maximum allowable discharge concentration of phenol varies from country to country, but generally it is about 10 mg / l (Yamada et al., 2005). According to the Ordinance on Hazardous Substances in Water (Official Gazette of SRS, no. 31/82) the maximum content of phenol in the waters of categories I and II is 1 mg / l, while in the waters of categories III and IV the limit is 300 mg / l.

Conventional methods for removing phenolics from wood industry WW include biological degradation, solvent extraction, adsorption and chemical oxidation(Hameed & Rahman, 2008; H. Jiang et al., 2003; Nair et al., 2008).

Biological treatment is economical and environmentally friendly method but at high concentrations of phenol, application of this method is not possible because of the inactivation of microorganisms. Other disadvantages are necessity of large land area and long time for microbial degradation, which makes this process less flexible in design and operation (Pinto et al., 2005; Rengaraj et al., 2002).

In the solvent extraction method the residual phenol concentration in wastewater barely meets the strict US Environmental Protection Agency (EPA) requirements (less than 1 mg/L in the wastewater). What is more, the separation of solute from the solvent is expensive and the loss of solvent requires additional treatment.

The adsorption process is proven to be efficient for the removal of organic contaminants and it is usually used only to treat dilute wastewater (Sharma, 2002; Waite & Gilbert, 1978). The most popular adsorbent is activated carbon due to its excellent adsorption abilities for phenolic compounds (Rengaraj et al., 2002). Drawback of this method is high initial cost; the regeneration of saturated carbons is also costly and results in loss of adsorbents. In addition, this treatment requires complexing agents to improve properties of activated carbon (Ahmaruzzaman, 2008).

One of the possible methods of phenol removal from aqueous environments is chemical oxidation by ferrate(VI), an environmentally friendly oxidant, coagulant and disinfectant (J. Q. Jiang & Lloyd, 2002).

2. Materials and Methods

As a starting material for the synthesis of ferrate from scrap iron, wastewater from the plant for corrosion of carbon steel is used. Other chemicals used are as follows: a solution of $Ca(ClO)_2$, 99%, 85% KOH, 99% NaOH, n-C_5H_{12} 99%, 96% C_2H_5OH, $(C_2H_5)_2O$ 99.5%.

Due to the fact that the concentration of Fe in used wastewater was high, 133 g/L, a drying process at 85°C will produce a precipitate containing mostly hydrated $FeCl_2$ and a smaller proportion of hydrated $FeCl_3$.

K_2FeO_4 was synthesized by using the obtained residue as a raw material. After drying, grinding of the solid residue was performed to obtain a larger reactive surface area. A rotating ball mill was formed in the laboratory, (Fig 1), to which in addition to the resulting ground residue added was $Ca(ClO)_2$ 99% in solid form and KOH 85% in solid form in relation to: solid residue : $Ca(ClO)_2$: KOH, 1 : 2: 3. The mixing is carried out in a ball mill, at a speed of 80 rotations per minute for 3 hours.

Since the reaction is exothermic, if necessary, cooling is performed from the outside of the mill. The resulting mixture was cooled in an ice bath, and then sequentially washed with 0.5 ml of n-pentane, methyl alcohol and ethyl ether for about 2 min. The solids on the filter paper were then dried in a vacuum furnace under pressure <30 mm Hg at room temperature for one hour to give a dry, K_2FeO_4. The resulting K_2FeO_4 is of technical quality, and for a purer ferrate it needs recrystallization i.e. dissolving of NaOH and re-deposition using KOH. The obtained K_2FeO_4 yield was determined by the chromite method (Waite & Gilbert, 1978).

In the second part of the experiment, the possibility of using ferrate synthesized from scrap iron in the treatment of waste water from a wood processing plant was examined.

Figure 1. Appearance of the rotary ball mill, in which the reactions take place.

Two wastewater samples from the wood processing plant were used in the experimental work: a sample from the thermal dryer and a sample from the steam chamber. The initial concentration of phenol in the sample from the thermal dryer was 27 mg / l and in a sample from the steam chamber 30 mg / l. This wastewater is characterized by a high content of natural organic matter. Chemical oxygen demand (COD) of the sample from the thermal dryer was 3233.1 mg O2 / l and of the sample from the steam chamber 4692.1 mg O2 / l. pH value of the sample from the thermal dryer was 4 and pH value of the sample from steam chamber was 5. the samples were treated with the solution of electrochemically synthesized ferrate(VI) concentration of 8 g / l in molar ratio phenol : ferrate(VI) = 1 : 5. The process of electrochemical synthesis of the alkaline solution of ferrate(VI) was based on transpassive anodic dissolution of iron alloys in a 10 M NaOH solution, in accordance with previous studies (Čekerevac et al., 2010; Nikolić-Bujanović et al., 2012) and it was carried out in a laboratory facility for electrochemical synthesis of ferrate(VI). The change in the concentration of phenol and COD value of the samples were determined using standard methods at MOL Institute, Stara Pazova.

The resulting $Fe(OH)_3$ needs to be annealed at 700°C to remove the pollutants which it precipitated as a coagulant, especially if they are organic compounds. Further procedure is in a ball mill, as previously described.

3. Results and Discussion

As reported in literature (Wei et al., 2015), iron sources for use in the process of dry and wet oxidation for Fe(VI) synthesis are mostly iron chloride and iron nitrate. Among them the iron nitrate is preferred because of the characteristics of fast dissolving and quick chemical reactions with hypochlorite to form Fe(VI). The rate of oxidation of iron chloride using hypochlorite is relatively low, since chloride ions which are released from the iron chloride will slow down the rate of dissociation of hypochlorite, which prolongs the time of Fe(VI) synthesis (Jiang et al., 2012). However, iron chloride will cost much less than iron nitrate.

Using the ratio of the reagent as an example, the ratio between the prices of these iron compounds (per unit of iron) was approximately (iron(III)chloride) : (iron(II)chloride) : (iron(III) nitrate), 1.0: 1.25 : 2.5. However, the goal of the study was to demonstrate the possibility of using wastewater from the steel pickling plant. According to data (Wei et al., 2015), wastewater from pickling steel contains many kinds of heavy metals and their concentrations are significantly higher than the legally permitted for wastewater. Heavy metals include Cr, Bi, Tl, Cd, Co, Cu, Ni, Pb and Zn. Fe and Cl are the most prevalent components, wherein Mn and Ca (respectively 1.386 and 1.551 g/L) are the second most numerous elements. In general, when the Fe content in the solution for pickling steel reaches 70-100 g/L, the solution is not used further in the process of etching of steel (Agrawal & Sahu, 2009).

It is obvious that the solution for pickling is used up to the Fe content of 133 g/L.

As the sum of Fe and Cl, 485 g/L is a third of the solution mass of 1.0 L (i.e., 1.4 kg), only a small amount of heat is required for the evaporation of its liquid components, including water and HCl. The solution is evaporated at a temperature of 85°C. The resulting precipitate was refined by grinding in order to obtain a large reactive surface during the mixing with $Ca(ClO)_2$, and KOH. In the Figure 1 is shown a ball mill with an electric motor in which the reactants were mixed and in which the reactions took place. Mixing was performed at a speed of 80 rotations per minute for 3 h.

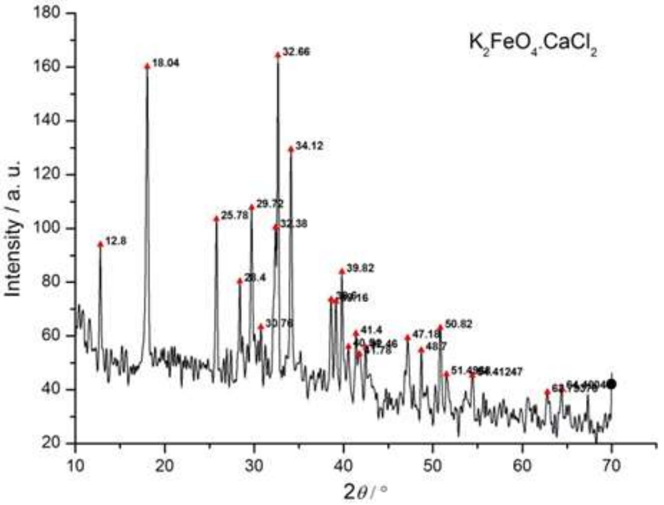

Figure 2. X-ray diffractogram of K_2FeO_4 admixture with $CaCl_2$.

The process that takes place during mixing in the ball mill can be represented by the following chemical reaction:

$$FeCl_2\ x\ 4H_2O + Ca(ClO)_2 + 2KOH \rightarrow K_2FeO_4 + CaCl_2 + 2HCl + 4H_2O \quad (2)$$

$$2FeCl_3\ x\ 6H_2O + 3Ca(ClO)_2 + 4KOH \rightarrow 2K_2FeO_4 + 3CaCl_2 + 3Cl_2 + 8H_2O \quad (3)$$

$$2FeCl_3\ x\ 6H_2O + 3Cl_2 + 8KOH \rightarrow 2K_2FeO_4 + 4KCl + 8HCl + 6H_2O \quad (4)$$

The process is exothermic and cooling is needed from the outside although the released water during the reaction lowers the temperature of the process. After the completion of mixing and cooling the resulting mixture in an ice bath, rinsing in organic solvents is conducted, and then drying in a vacuum dryer at room temperature. The obtained precipitate is dark purple in color proving the presence of Fe(VI), as confirmed by x-ray diffractometer. X-ray diffractogram of potassium ferrate (VI), (Fig. 2), is in good correlation with diffractograms presented in relevant literature (Xu et al., 2007), which has confirmed purity of this reactant.

This method provides K_2FeO_4 of sufficient purity for use in the treatment of wastewaters of different origin. The yield of ferrate salt is calculated from the following equation:

$$yield(mol\%) = \frac{(K_2FeO_4\ product\ weight) \times (product\ purity)\ \times\ (Fe\ atomic\ weight)}{(K_2FeO_4\ molecular\ weight) \times (Fe\ mass\ in\ the\ solid\ derived)} \quad (5)$$

The analysis of the obtained ferrate salt showed a purity of 82 wt. % while the yield was 15 Mol. %, which, given that waste Fe is used, it is more cost-effective than any other method of synthesis of ferrate from iron or its alloys.

The basic idea of this study was the use of $Fe(OH)_3$ as raw material for the synthesis of ferrate. Ferrous hydroxide occurs as a product in the reduction of ferrate in the reaction with the pollutants as their coagulant in wastewater treatment. The formed precipitate could be used for the recovery of ferrate using the process described in this paper according to the given reactions 6 and 7:

$$Fe(OH)_2(s) + 2ClO^- + 2OH^- \rightarrow FeO_4{}^{2-} + 2Cl^- + 2H_2O \quad (6)$$

$$2FeO(OH)(s) + 3ClO^{-} + 4OH^{-} \rightarrow 2\ FeO_4{}^{2-} + 3Cl^{-} + 3H_2O \quad (7)$$

Results of phenol removal by ferrate(VI) from the samples of wastewater from the thermal dryer and steam chamber are shown in Table1.

Table 1. Reduction of the phenol concentration in the samples of wastewater from the thermal dryer and steam chamber before and after the treatment.

	Phenol concentration in the untreated sample, mg / l	**Phenol concentration in the treated sample, mg / l**	**Removal efficiency, %**
Thermal dryer	27	6,79	74,9
Steam chamber	30	8,20	72,7

The results of the treatment shows high removal efficiency of phenol by ferrate(VI), 74.9% and 72.7%, for wastewater from thermal dryer and steam chamber, respectively, Table 1. Phenol is removed from aqueous solution by flocculation and coagulation with ferrous hydroxide, reactions, Figure 3, which is obtained as a product of ferrate(VI) reduction and has a very developed absorption area(Jiang & Lloyd, 2002). Since ferrous hydroxide has an extremely low solubility in these conditions, presence of residual Fe is not expected.

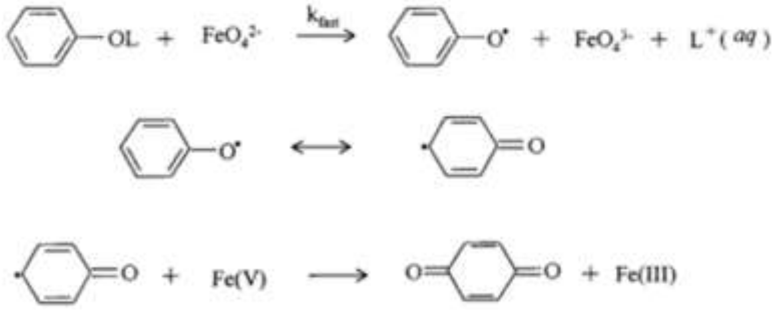

Figure 3. Removal of phenol from water using ferrate(VI).

Possibility of phenol removal using ferrate(VI) was additionally confirmed by determining the value of COD in the samples treated by ferrate(VI), Table 2.

Table 2. Percentage of COD removal during oxidation reaction of phenol by ferrate(VI)

	COD of untreated sample, mgO$_2$ / l	**COD of treated sample, mgO$_2$ / l**	**Reduction efficiency of COD, %**
Thermal dryer	3233.1	2384	26.3
Steam chamber	4692.1	2594	44.7

After the addition of ferrate(VI) into the solution, Figure 4, showed a COD reduction of4692.1 mgO$_2$ / l, for thermal dryer WW and steam also characterized by high initial COD values, 3233.1 and 26.3 % for thermal dryer and 44.7 % for steam chamber.

Using higher doses of ferrate(VI) could reach a more efficient reduction of COD values which requires further optimization of the treatment process of WW from wood industry by ferrate(VI)

The resulting precipitate was subjected to treatment according to the described method. After cooling and examination, the precipitate acquired a purple color, which indicates the presence of ferrate. Chromite analysis determined the presence of 70 wt.% K_2FeO_4.

4. Conclusion

This paper presents the recycling of wastewater from the process of pickling steel which in itself besides iron contains a large percentage of other heavy metals. The core of this work was to use the present $FeCl_2$ and $FeCl_3$ as raw materials for getting K_2FeO_4.

Figure 4. Sample of WW from the steam chamber before the treatment and after the second step of the treatment by ferrate (VI).

Using the rotary ball mill the synthesized K_2FeO_4 has a purity of 82 wt. % with a yield of 15 Mol. %.

The resulting reaction product was a dark purple color which indicates the presence of ferrate, and x-ray diffraction confirmed it. Showed was that with this procedure it is possible to round off the process of synthesis and use of ferrate(VI) because the product formed in the process of wastewater treatment, $Fe(OH)_3$, can be recycled and from it derive ferrate(VI) again.

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Primena otpadnog gvožđa u sintezi ferata(VI) i uklanjanje fenola kao potvrda efikasnosti

Ljiljana Nikolić Bujanović[1, *], Milan Čekerevac, Miloš Simičić, Milena Tomić[2]

[1]Fakultet za ekologiju i zaštitu životne sredine, Univerzitet Union-Nikola Tesla, Beograd, Srbija
[2]IHIS Techno-experts, Istraživački i razvojni centar, Batajnički put 23, Beograd, Srbija

*Autor za korespondenciju: ljnikolicbujanovic@unionnikolatesla.edu.rs, bujanovic08@gmail.com

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Abstrakt: Ferat (VI) je jako oksidaciono, koagulaciono i flokulaciono sredstvo. Zbog svojih karakteristika pogodan je za tretman voda različitog porekla. U ovim procesima nastaje ekološki i netoksičan proizvod, $Fe(OH)_3$, koji se prema rezultatima ovog rada može reciklirati i ponovo sintetizovati u ferat(VI). U ovom radu je prikazana metoda za sintezu feratnih soli postupkom oksidacije iz otpadnih voda od nagrizanja čelika koje sadrže soli $FeCl_2$ i $FeCl_3$.

Metoda za sintezu podrazumeva proces oksidacije fero i feri jona pomoću $Ca(ClO)_2$ u prisustvu KOH u čvrstom stanju. Snimak rendgenskog difraktometra pokazuje značajno prisustvo K_2FeO_4, dok je analiza pokazala prinos od 15%.traž

Prikazana je primena ferata sintetizovanog iz otpadnog gvožđa u procesu prečišćavanja otpadnih voda iz drvne industrije. Primer koji je dat u ovom radu je tretman uzoraka WW iz drvne industrije, iz termo sušare i parne komore, primenom Jar testa. Početna koncentracija fenola u uzorku iz termičke sušare iznosila je 27 mg/l, a u uzorku iz parne komore 30 mg/l. Ova otpadna voda takođe ima visok sadržaj prirodne organske materije (HPK uzorka iz termo sušare je 3233,1 mgO_2/l i HPK uzorka iz parne komore 4692,1 mgO_2/l). Efikasnost uklanjanja fenola feratom(VI) iznosila je 74,85% i 72,67% za uzorke iz termičke sušare i parne komore, respektivno.

Ključne reči: kalijimferat, ferohlorid, ferihlorid, fenol, x-rey

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