HUMIC ACID REMOVAL FROM WATER WITH FENTON

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Abstract
The aim of the research was to reduce the concentration of humic acid in water solutions. We have found that the Fenton's reaction was suitable for the treatment of synthetic wastewater with humic acid. The maximum reduction of COD for the treatment of wastewater with humic acid stood at 97.4 %, achieved at following conditions: 0.2 g $FeSO_4$, *pH* = 3 and reaction time 40 min. The maximum reduction of COD was achieved if the pH of water solution was adjusted to 3 before the treatment with Fenton reagent.

Introduction
Many wastewater including compost leachate contain humic acids. [1] Leachate could pollute the underground water sources. Surface and wastewaters are many times polluted by humic acids, heavy metals, xenobiotic and inorganic macro-compounds, such as ammonium and iron compounds from leachate [2]. Also phthalates and poly-chloro-bi-phenyls from pesticides and plastic parts were measured in increased concentrations especially in wastewaters. The limit concentration of humic acid in drinking water sources is 0.1-10 mg/L. However, if humic acid reacts with chlorine during disinfection toxic dihalo-acetonitrile (DHAN) could be formed [3]. Advanced oxidation processes are very efficient for water treatment if the pollutants are very persistent. Among them Fenton reagent could be efficient for degradation of e.g. dyes [4]. Fenton reagent is the reaction with the combination of either Fe^{2+}andH_2O_2 or H_2O_2/Fe^{2+}/UV-rays. Hydroxyl radicals are formed at room temperature. Fe-ions represent catalyst, while H_2O_2 represents oxidation agent. Advantages of Fenton in combination of $Fe^{2+}$and H_2O_2 are low energy demand, low toxicity of chemicals, high reaction rate, high oxidation rate and simple equipment [1, 5]. Wu et al [6] found that Fenton reagent is very important for humic acid degradation. The main drawback of Fenton process is sludge formation [7]. It is assumed that up to 50 % more sludge is formed.

In the present work the effects of Fenton reagent on organic removal from water solution was investigated. Iron sulphate in combination of hydrogen peroxide were used in experiments. The concentrations, ratio between both chemicals, the reaction time and pH influences were studied. It was found that Fenton reagent is efficient in humic acid degradation.

Experimental
Humic acid is soluble in alkaline solutions, while at pH less than 2 it could be decomposed. Humic acid is formed from many molecules which are bounded with hydrogen and hydrophobic bonds. Humic acid was purchased by Sigma Aldrich (Germany). Working solution of humic acid was prepared by mixing 1 g of humic acid with NaOH. For each experiment the initial concentration was 30 mg/L (Fig. 1), prepared by diluting working standard solution.

Figure 1. Standard humic acid solution

Table 1 represents the analytical methods used.

Table 1: The analytical methods

Parameter	Apparatus	Method
pH	WTW Multi 3410	ISO 10523
COD(mg/l O_2)	Thermoreactor Merck TR620	ISO 6060
Absorbance 254 nm	Spectrophotometer Agilent 8453	ISO 7887

The reaction between Fenton reagent and synthetic water was performed by different amounts of $FeSO_4.7\ H_2O$ at room temperature. It was found that the influence of temperature is negligible [1]. The mass of iron salt was chosen at 0.1 g, 0.2 g and 0.3 g. The molar ratio of $FeSO_4.7\ H_2O$: H_2O_2 was set to 1:3, 1:5 and 1:7. The reaction time was set to 20 mins, 40 mins and 60 mins. All parameters were chosen according to literature data [8]. If necessary pH was adjusted using 0,1 M HCl or 0,1 M NaOH.

Results and discussion

The results obtained for COD are presented in Fig. 2. The best removal efficiency was determined at 0.2 g of $FeSO_4$. The pH was measured at 10.7 due to the humic acid alkaline solution. It was prepared in NaOH for stability purposes. After the Fenton reagent addition, it decreased to 2.5 due to H_2O_2 from Fenton reagent.

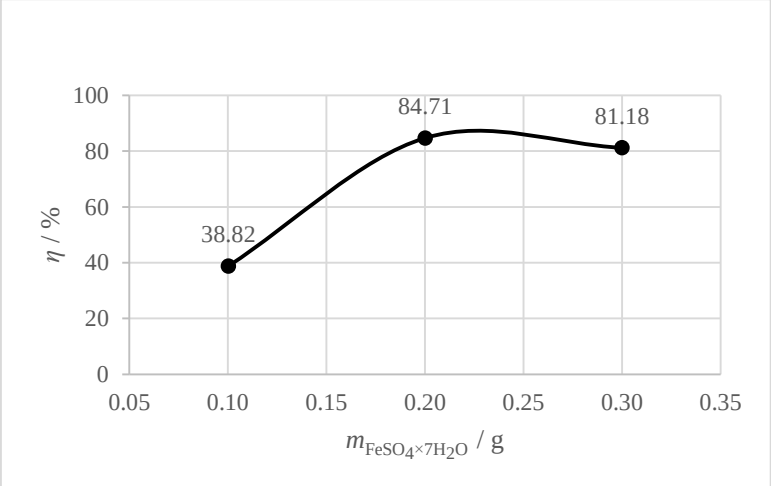

Figure 2. COD removal in dependence of amount of $FeSO_4$

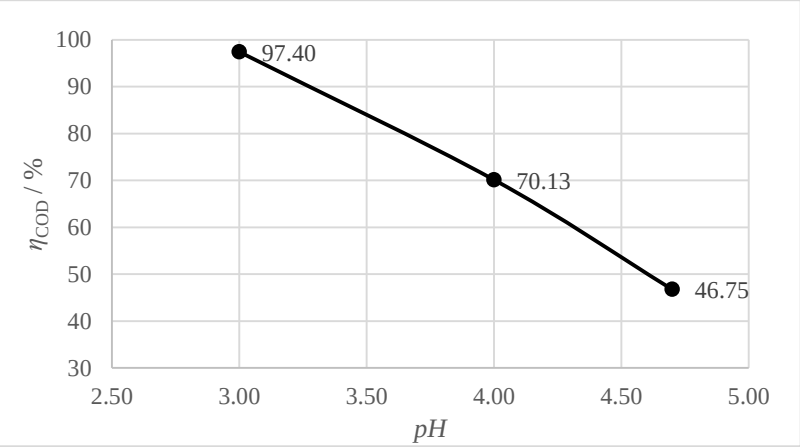

Figure 3. COD removal in dependence of pH

It was left as it was (pH = 4.7), then adjusted to pH = 3 and pH = 4. The best removal efficiency was achieved at pH = 3 at 97.4 % as seen from Fig. 3.

After the reaction the pH value was very similar of those solution where there was no pH adjustment. The optimum results were observed at the same values as discovered in another research [9].

The reaction time was varied from 20 mins to 60 mins. The results were very similar (not presented), with the similar removal after 60 mins at 95.7 %.

Conclusion

Humic acid removal from water solution using Fenton reagent was studied. The main parameter was chemical oxygen demand COD. The COD was mostly reduced in synthetically prepared water for 97.4 % with the 0.2 g of Fenton reagent per 100 ml of solution at the molar ration $FeSO_4$:H_2O_2 = 1:3. Very important is to adjust pH value to 3 before the reaction and that reaction last 40 mins**.**

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