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Decolorization of Secondary Effluent from Piggery Wastewater by Fenton Reaction Using Iron Powder

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Abstract

A Fenton reaction using 150-μm iron powder for treating activated sludge from livestock-raising wastewater resulted in significant decreases in chromaticity and chemical oxygen demand. The optimum weight ratio of H_2O_2/Fe(0) was 0.3, and the optimum initial pH and the optimum reaction time were 3.5 and 30 mins. Under these optimum conditions, the removal ratios of chemical oxygen demand and the chromaticity of the supernatant after polymer coagulant addition and precipitation of the sludge in a continuous miniplant experiment were 86% and 84%, respectively.

Keywords: decolorization, heterogeneous Fenton, chemical oxygen demand, iron powder

1. Introducation

Since dairy production has increased in recent years, the quantity of livestock excrement has also increased. As a result, the proper management of animal wastes has become difficult, and there has been an increase in the number of cases of waste mismanagement. In Japan, regulations require emissions of a certain size to be treated before discharge into public waters. Although urea in pig or cattle excrement is processed using activated sludge or anaerobic treatments, the final effluent is often dark brown in color, and in many cases this gives the impression that the excrement was discharged without complete treatment. Post-biological physicochemical treatments for chromaticity or chemical oxygen demand (COD_{Mn}) removal from waste fluids include electro-coagulation processes (Yetilmezsoy et al., 2009) and Fenton methods (Lee & Shoda, 2008). In this study, we focused on the Fenton reaction as a proven decolorization method. The Fenton reagent, a mixture of ferric ion salts with hydrogen peroxide (H_2O_2), can easily oxidize even refractory organics because it produces hydroxyl radicals for wastewater treatment very simply. The disadvantage of the Fenton reaction is that the added iron salts are retained in the process, causing additional water pollution (Lucking et al., 1998). Heterogeneous Fenton processes using zero-valent iron are therefore of particular interest since most of the iron remains in the solid phase (Aleksic et al., 2010). Nanosized zero-valent iron in particular has been found to increase the efficiency (Wang et al., 2010).

In this study, a decolorization system using a heterogeneous Fenton method with micro-sized non-supported iron powder is proposed and discussed. Segura et al. (2012) have explained the mechanism of the heterogeneous Fenton method using iron powder. When the pH is low, ferrous iron elutes from the iron powder under oxidizing conditions, as shown in Equation 1 (Chu et al., 2012).

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (1)$$

As shown in Equation 2, ferrous ions present within solid iron oxide under acidic conditions, are oxidized by

H_2O_2 to ferric ions, and hydroxyl radicals are generated at the same time.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \quad (2)$$

Ferric ions are then reduced to ferrous ions, and iron is oxidized to ferrous ions, as shown in Equation 3.

$$2Fe^{3+} + Fe0 \rightarrow 2Fe^{2+} + Fe^{2+} \quad (3)$$

In this study, to supply the required ferrous ions in the Fenton reaction solutions, we used iron powder dissolved under acidic conditions. Therefore, ferrous ions are sequentially converted to ferric ions, preventing the formation of excessive iron hydroxide, which occurs in homogenous Fenton methods.

2. Methods and Materials

2.1 Determination of Optimum Treatment Conditions

Iron powder (150 µm) and 30% (w/v) H_2O_2 (Wako Pure Chemical Industries Ltd., Osaka, Japan) were used. The effluent from the activated sludge facility of a wastewater plant at a piggery in Chiba-shi (Chiba Prefecture, Japan) was used as the raw water source in this study. Table 1 and Figure 1 show the characteristics of the wastewater and the relationship between chromaticity and COD, respectively. Decolorization treatment will therefore lead to a reduction in COD.

Table 1. Average water quality during experimental periods

	(Average)
pH	7.7~9.3 (8.0)
Chromaticity	460~740 (590)
COD (mg/l)	130~280 (180)
SS (mg/l)	10~230 (45)
BOD (mg/l)	20~160 (97)
T-N (mg/l)	30~350 (200)
T-P (mg/l)	50~100 (64)

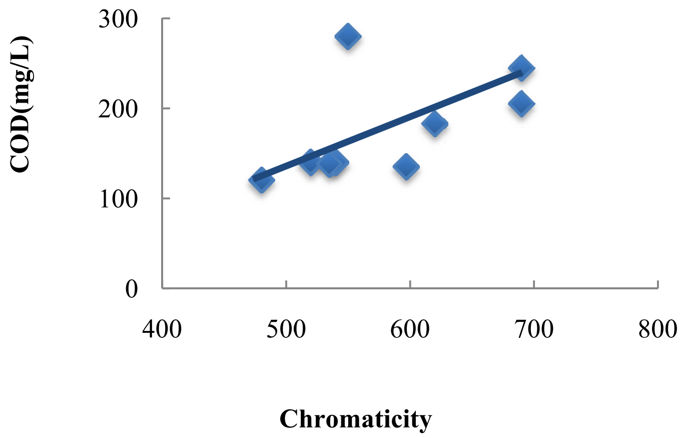
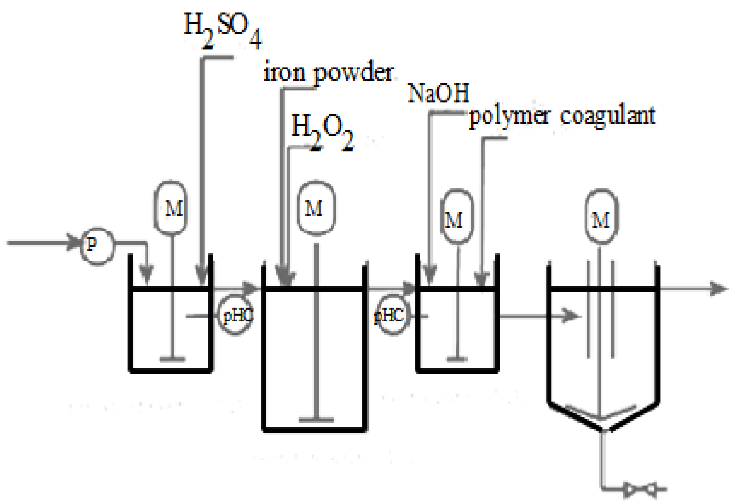


Figure 1. Relationship between chromaticity and COD

The Fenton method was applied to 200 mL of livestock wastewater in 500 mL flasks. All procedures were carried out at room temperature and the initial pH was adjusted to the desired pH using sulfuric acid. Then H_2O_2 (30% w/v) and iron particles were added to the flask and the mixture was stirred at 120 rpm. At the end of the operation, the pH was adjusted to 7–8 using NaOH. The effects of varying the different parameters of the Fenton reaction were then investigated. As shown in Figure 2, the laboratory-scale continuous processing system consists of a 1-L reaction vessel, a 0.5-L neutralization tank, and a 1-L precipitation tank. Raw water was supplied to the system at a flow rate of 1.0 L/h, and the pH of the reaction tank and neutralization tank were adjusted to 3.5 and 6.0, respectively, using 0.2 M sulfuric acid. In order to prevent the outflow of iron powder from the reaction tank, a baffle was fitted at the exit port. Iron powder (5 g) and 150 mg/L H_2O_2 (30% w/v) were added to the reaction vessel. Unreacted iron powder carried over from the reaction tank to the neutralization tank was removed and returned to the reaction tank. Accumulated sludge in the precipitation tank was periodically removed. The Method section describes in detail how the study was conducted, including conceptual and operational definitions of the variables used in the study, Different types of studies will rely on different methodologies; however, a complete description of the methods used enables the reader to evaluate the appropriateness of your methods and the reliability and the validity of your results, It also permits experienced investigators to replicate the study, If your manuscript is an update of an ongoing or earlier study and the method has been published in detail elsewhere, you may refer the reader to that source and simply give a brief synopsis of the method in this section.



P: pump; M: Moter; pHC: pH controller

Figure 2. Continuous processing experiment

2.2 Miniplant Experimental Procedure

The miniplant was installed at the site of a dairy farm in Chiba Prefecture; a schematic diagram of the miniplant system is shown in Figure 3, and the relevant capacities of the components are listed in Table 2. During the decolorization operation, the following continuous processes are performed. Raw water is acidified in a pH control tank using sulfuric acid. In the next reaction vessel, the Fenton reaction is performed by supplying and agitating H_2O_2 and iron powder. This reaction uses 0.25 g/L iron powder of mean particle size 150 µm; the pH and H_2O_2 concentration were kept at 33.5 and 150 mg/L, respectively. In the next tank, i.e., the neutralization tank, the pH is adjusted to neutral and a polymer coagulant is added. The amount of coagulant added depends on the suspended solids level.

2.3 Analytical Methods

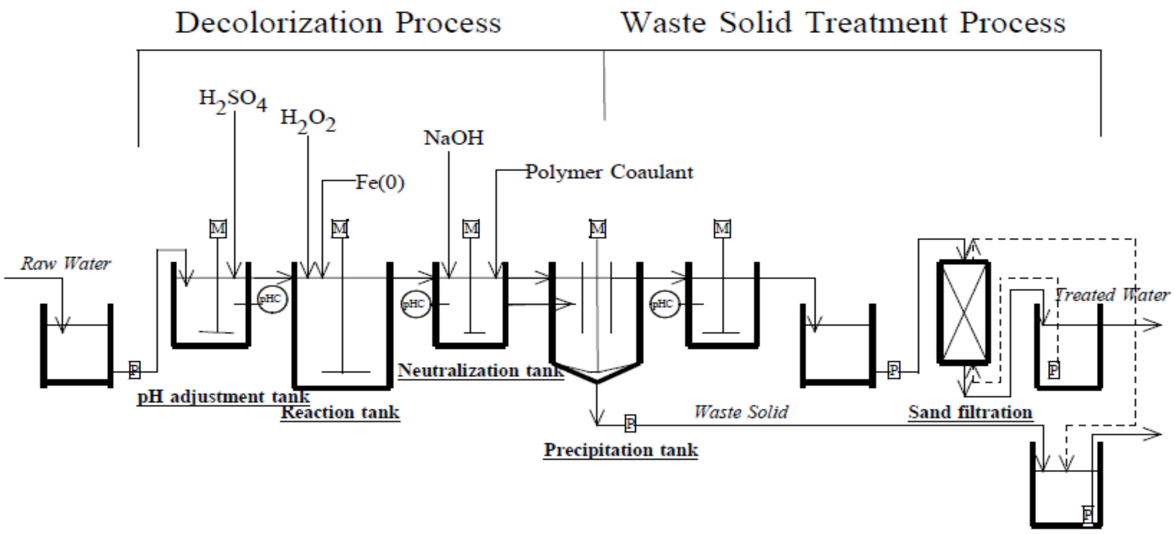
COD_{Mn}, biochemical oxygen demand (BOD), suspended solids, total N (T-N), and total P (T-P) were analyzed based on the sewer test method (Japan Sewage Works Association, 1997), and the chromaticity was analyzed using a spectrophotometer (V530, JASCO, Tokyo, Japan) after filtering the supernatant through a 0.45-µm filter. The absorbance of the sample was detected at 390 nm, and the color removal ratio was calculated as the difference between the initial and final absorbances divided by the initial absorbance. The pH was measured using a standard laboratory pH meter (D-52, Horiba, Kyoto, Japan).

3. Results and Discussion

3.1 Determination of Optimum Treatment Conditions

The influence of pH on chromaticity is shown in Figure 4. After 60 min, the chromaticity decreased to 58% of that of the raw water at pH 3.2. This is a result of humic acid being condensed. There is very little reaction at pH

5.9 and pH 4.5. It is therefore necessary to increase the initial pH of the raw water to 3–3.5 to achieve an effective heterogeneous Fenton reaction. There is very little reaction at pH 5.9 and pH 4.5. It is therefore necessary to increase the initial pH of the raw water to 3–3.5 to achieve an effective heterogeneous Fenton reaction. Shimizu et al. (2012) reported a large reduction in total organic carbon at a pH of 3 for decomposition of phenol using 75-µm iron powder. In this research, we used 150-µm iron powder, which gave effective decolorization and decreased the COD (Martins et al., 2012). These results indicate that micron-sized iron powder can be used practically in heterogeneous Fenton reactions. The relationship between chromaticity and the ratio of $H_2O_2/Fe(0)$ at pH 3.5 is shown in Figure 5. As the molar ratio increased, the chromaticity removal rate increased to a maximum of 78% at a molar ratio of 0.3. In previous research by Lee and Shoda (2008), the Fenton method was used for removal of COD and color from high-strength livestock waste, and the optimum molar ratio of H_2O_2/Fe^{2+} was found to be 2.



P: pump; M:Moter; pHC: pH controller

Figure 3. Diagram of miniplant

Table 2. Effective volume of each reactor in the miniplant

	Effective Volume
pH adjustment	$0.2m^3$
Reaction tank	$2.0m^3$
Neutralization tank	$0.2m^3$
Precipitation tank	$0.2m^3$
Sand filtration	400φ×1500h

The water quality data for the raw water and treated water at 6 h in the continuous experiment are shown in Table 3. The chromaticity and COD extraction ratios were 87% and 85%, respectively. The suspended solids removal rate was 89%, and as 18 mg/L of the suspended solids in the treated water remained, it was still a little colored. It is thought that complete removal of the outflow suspended solids is required to give complete decolorization. The T-N and T-P removal rates were about 12% and 100%, respectively. The amount of waste sludge removed over 6 h of operation was 0.5 g/L. Although the concentration of iron powder decreases during elution, a stable continuous reaction can be achieved by the addition of a corresponding amount of fresh iron powder.

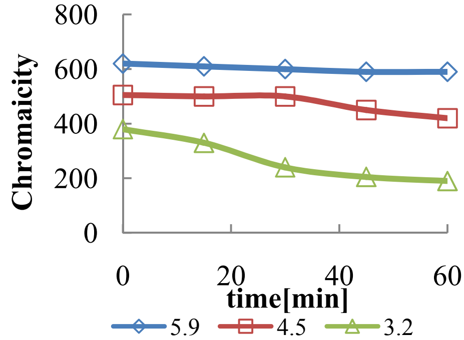


Figure 4. Effects of initial pH on chromaticity

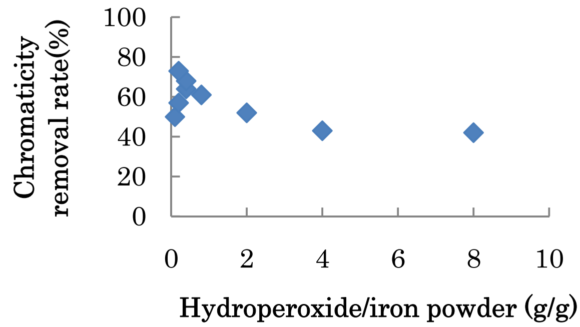


Figure 5. Effects of hydroperoxide/iron powder ratio

Table 3. Water quality data after 6 h of continuous treatment

	Raw Water	Treated Water
pH	5.7	6.0
Chromaticity	653	84
COD (mg/L)	395	61
SS (mg/L)	165	18
T-N (mg/L)	525	462
T-P (mg/L)	34	1

3.2 Miniplant Experiment

The treatment condition was 1015 m^3/day of actual drainage. Over the period of the experiment, the raw water, treated water, and final effluent were measured with respect to COD, chromaticity, and suspended solids; the values are shown in Figures 6–8. The average results over 150 d using the Fenton reaction are shown in Table 4. The chromaticity of the treated water is generally about 100, except for a couple of instances. These higher values were caused by higher raw water COD (day 11), addition of less iron powder (at approximately day 50), and addition of less H_2O_2 (after day 90). A part from the spiked values, the average COD values of the raw and treated water were about 180 mg/L and 29 mg/L, respectively. In order to maintain this value in the treated water, 150 mg/L of H_2O_2 and 0.25 g/L of iron powder were needed. Up to day 67, no polymer coagulant was added and the suspended solids of the effluent at times exceeded 100 mg/L, so from day 67, 5 mg/L of polymer coagulant were added, and the suspended solids decreased to 10 mg/L. Sand filtration is unnecessary if a polymer coagulant is added. The T-P of the raw water was 50–100 mg/L, but in the treated water it was less than 1 mg/L. The total amount of waste sludge removed from the process was about 0.6 kg/m^3. There have been a few reports on the characteristics of processing using iron powder. Most experiments were performed to determine the operating conditions using the batch method.

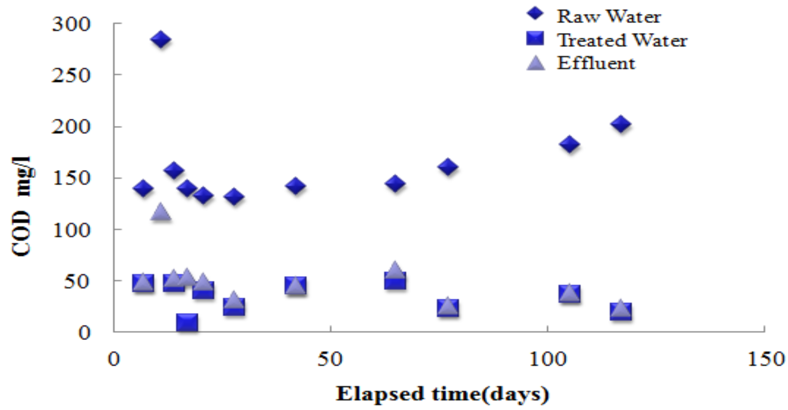


Figure 6. Changes in chromaticity over the duration of the experiments

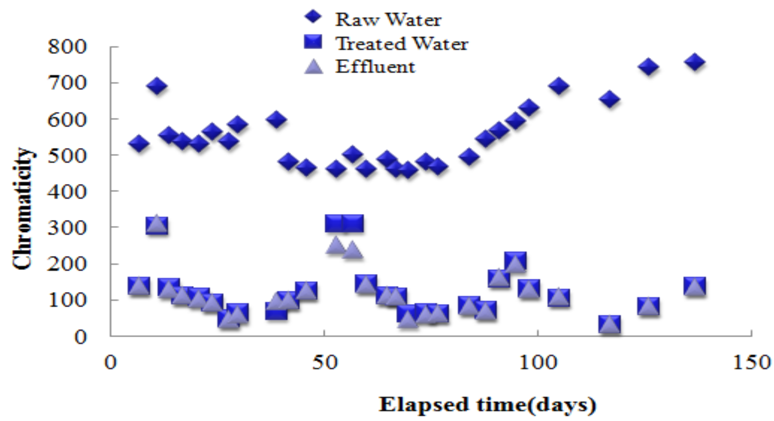


Figure 7. Changes in COD over the duration of the experiments

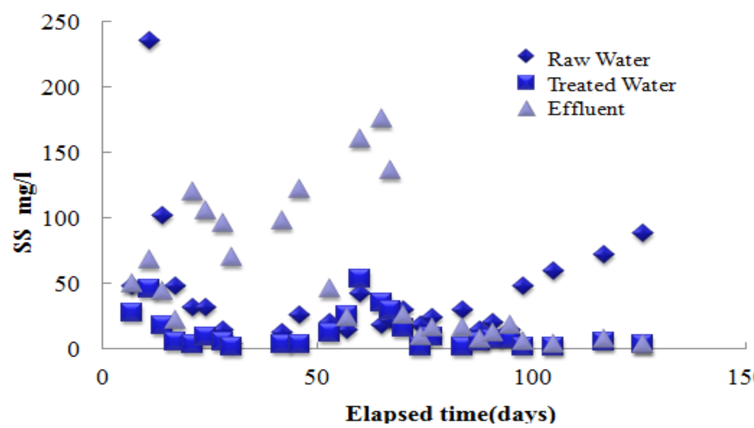


Figure 8. Changes in suspended solids over the duration of the experiment

Table 4. Average result over 150 d using a heterogeneous Fenton reaction

	Raw Water	Treated Water	Removal Rate (%)
Chromaticity	590	80	86
COD (mg/L)	180	29	84
SS (mg/L)	45	5.0	89
T-N (mg/L)	97	5.2	95
T-P (mg/L)	64	0.7	99

4. Conclusion

In this study, we investigated the decolorization of piggery effluent using the heterogeneous Fenton reaction. Even if micro-sized zero-valent iron powder was used, an adequate decolorization rate and COD extraction ratio were achieved. Although some SS are contained in the effluent, the problem of fine particles was solved by using a polymer coagulant.

References

Aleksic, M., Kusic, H., Korpivanac, N., Leszcynska, D., & Bozic, A. L. (2010). Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water–The applicant of zeolite assisted AOPs. *Desaliniation, 257*(1-3), 22-29. http://dx.doi.org/10.1016/j.desal.2010.03.016

Chu, L., Wang, J., Dong, J., liu, H., & Sun, X. (2012).Treatment oc coking wastewater by an advanced Fenton oxidation process using irpn powder and hydrogen peroxide. *Chemosphere, 86*, 409-414. http://dx.doi.org/10.1016/j.chemosphere.2011.09.007

Japan Sewage Works Association. (1997). Sewage water testing method.

Lee, H., & Shoda, M. (2008). Removal of COD and color from livestock wastewater by Fenton method. *Journal of Hazardous Materials, 153*, 1314-1319. http://dx.doi.org/10.1016/j.jhazmat.2007.09.097

Lucking, F., Koser, H., Jank, M., & Ritter, A. (1998). Iron powder,graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxidein aqueous solution. *Water Research, 32*(9), 2607-2614. http://dx.doi.org/10.1016/S0043-1354(98)00016-5

Martins, R. C., Lopes, D. V., Quina, M. J., & Quinta-Ferreira, R. M. (2012). Treatment improvement of urban landfill leachates by Fenton-like process using ZVI. *Chemical Engineering Journal, 192*(1), 219-225. http://dx.doi.org/10.1016/j.cej.2012.03.053

Segura, Y., Martínez, F., Melero, J. A., Molina, R., Chand, R., & Bremner, D. H. (2012). Enhancement of the advanced Fenton process (Fe0/H_2O_2) by ultrasound for the mineralization of phenol. *Applied Catalysis B: Environmental, 113-114*, 100-106. http://dx.doi.org/10.1016/j.apcatb.2011.11.024

Shimizu A., Tokumura, M., Nakajima, K., & Kawase, Y. (2012). Phenol removal using zero-valent iron powder in the resence of dissolved oxygen: Roles of decomposition by the Fenton reaction and adsorption/precipitation. *Journal of Hazardous Materials, 201-202*, 60-67. http://dx.doi.org/10.1016/j.jhazmat.2011.11.009

Wang, W., Zhou, M., Mao, Q., Yue, J., & Wang, X. (2010). Novel NaY zeoloite-supported nanoscale zero-valent iron as an efficient heterogeneous Fenton catalyst. *Catalysis Communications, 11*(11), 937-941. http://dx.doi.org/10.1016/j.catcom.2010.04.004

Yetilmezsoy, K., Ilhan, F., Sapci-Zengin, Z., Sakar, S., & Gonullu, M. T. (2009). Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: A post-treatment study. *Journal of Hazardous Materials, 162*(1), 120-132. http://dx.doi.org/10.1016/j.jhazmat.2008.05.015