

IN-SITU CHEMICAL OXIDATION USING HYDROGEN PEROXIDE FOR THE TREATMENT OF GROUNDWATER

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ABSTRACT: In-situ Chemical Oxidation (ISCO) is the emerging technology used for site remediation. Four different oxidants are being used for this technology, i.e., Hydrogen peroxide, Ozone, Permanganate and Persulfate. Mostly being used is catalyzed hydrogen peroxide among all because of its efficiency to remediate and is also less costly. The objective of this paper is remediate groundwater sample using Catalyzed Hydrogen Peroxide. Different concentrations of peroxide were tested along with Sodium Hypochlorite. The present study showed that catalysed hydrogen peroxide can be effective to decolorize and demineralize the groundwater and used for site remediation. The experimental results indicate that during Fenton's oxidation, decolourization was faster than degradation. The rate of oxidation was influenced by dose of Fe^{2+} , H_2O_2 , and sodium Hypochlorite. The optimum conditions required for maximum degradation were 1.5g/L of sodium hypochlorite, 0.5g/L of H_2O_2 and accordingly Fe^{2+} dose. Fe^{2+} added is 5-25 parts wt/wt to hydrogen peroxide. This investigation has demonstrated the potential of applying Fenton's process for the treatment of groundwater.

KEYWORDS: In-situ chemical oxidation, Groundwater treatment, Site remediation, Oxidation, Hydrogen Peroxide, Sodium Hypochlorite.

1. INTRODUCTION

Environmental aspects of groundwater resources have become a prime concern. The major source for drinking as well as agriculture and industrial activities is ground water. Infiltration/ percolation of waste chemicals used in various manufacturing processes have turned the groundwater polluted. The quality of groundwater resources globally has been under serious threat due to their exposure to a broad spectrum of contaminants emanating from a variety of sources including agricultural systems, industries and mines (Tase, 1992; Schipper et al., 2010; Wiafe et al., 2013; Rodak et al., 2014). The treatment of groundwater has become necessary. The pollutants and contaminants in groundwater can be removed/ treated by applying various physical, chemical and biological technologies thereby making it safe for use.

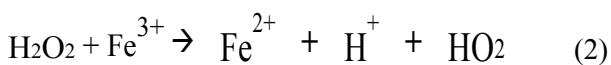
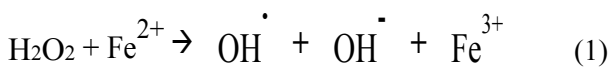
The conventional technology used to remediate contaminated groundwater has been the 'pump-and-treat' (P&T) systems. However, clean-up goals have hardly been met with this technique (Henderson and Demond, 2007). Subsequently, bioremediation was the primary remediation process used throughout the 1980s and much of the 1990s. Numerous other site remediation processes have been used for the saturated and unsaturated zones. Saturated zone technologies include air sparging and permeable reactive barriers, and common technologies for the unsaturated zone include soil vapour extraction and bioventing (Richard J. Watts et al, 2006). Permeable reactive barriers (PRBs) are one of the innovative technologies being used for in situ remediation of contaminated groundwater (Tratnyek, 2002; USEPA, 2002).

SR. NO.	WELL ID	pH	COD (mg/L)	BOD (mg/L)	TDS (PPM)	CHLORIDES (mg/L)	COLOR (CU)
1.	602A	7.75	230	150	5740	120	3160

Table no. 1: Characteristics of Groundwater Sample

Like most remediation technologies, each of these has limitations, which generally fall into two categories: (1) Reactivity with contaminants of concern and (2) mass transfer of contaminants from the sorbed phase and dense non-aqueous phase liquids (DNAPLs) to the medium in which the reactive species exists, usually water (Watts, 1998). In the 1990s, the first reports were published on in situ chemical oxidation (ISCO) (Watts et al. 1990; Schnarr and Farquhar, 1992). ISCO is the delivery of strong chemical oxidants to the subsurface for the purpose of treating organic contaminants. The first ISCO process that was investigated in laboratory research and developed at full scale was catalyzed H₂O₂ propagations (CHP), commonly known as modified Fenton's reagent (Watts et al. 1990; Tyre et al., 1991). Shortly following the initial use of Fenton's reagent, ozone sparging and permanganate treatment came into widespread use alone or in combination with others. (Siegrist et al., 2001; Parmila Devi, 2016). Recently, persulfate as a chemical oxidant has been found to be promising for in situ remediation of recalcitrant organic contaminants in groundwater and soil (Yong Qing Zhang et al., 2010).

Most commonly used chemical oxidant is catalysed hydrogen peroxide (CHP), which works as shown in following reaction (Lauren L. Bissey et al, 2006; K. Swaminathan et al, 2003):



The process is based on the catalyzed decomposition of hydrogen peroxide by soluble iron, iron chelates, or iron minerals to generate the strong oxidant

hydroxyl radical (OH[•]), as well as other reactive oxygen species. The nature of the catalyst used, the pH, and the hydrogen peroxide concentration are some of the important process parameters that are to be kept in mind while using peroxide in ISCO (Richard J. Watts et al, 2006). The iron oxide minerals naturally present in the subsurface serve as effective CHP catalysts (Tyre et al., 1991). Soluble iron and iron minerals are most effective at acidic pH, and iron chelates are also effective at neutral pH regimes.

If iron minerals are used as the CHP catalyst, the pH must be maintained at less than 4.0. Hydrogen peroxide concentrations in the 2–12% (0.6–3.6 M) range are typically used for ISCO applications (Richard J. Watts et al, 2006).

The present study attempts to use Fenton's reagent to treat the groundwater ejected from a well ID-602A, which has the characteristics shown in table no. 1.

2. MATERIALS AND METHODS

2.1. Reagents

Hydrogen peroxide (30%), Sulfuric acid (98%), Citric acid (99.5%), Ferrous sulfate heptahydrate (98%), sodium hypochlorite powder (32% chloride) and sodium hydroxide pellets (≥97%) were used of analytical grade.

2.2. Experimental Setup

All the experiments were conducted in 50mL, 100mL and 250mL borosilicate beakers used as reactors covered with aluminium foils. A known volume of groundwater sample was taken in the reactor. Predetermined quantity of sodium hypochlorite, i.e. 1.5g/L was added in the reactor and put on continuous stirring for about half hour. After the precipitates settles, the sample was tested with different dosing of 30% hydrogen peroxide i.e. 0.25g/L, 0.5g/L and 0.75g/L, with ferrous sulfate addition and stirred using magnetic stirrer. All the experiments were carried out without any pH adjustment. Hydrogen peroxide and ferrous sulfate were added from the stock solution initially prepared. Fe²⁺ added is 5-25 parts wt/wt to hydrogen peroxide. After reactions completed, samples were filtered through 0.45 lm filter paper and immediately analysed.

2.3. Analysis

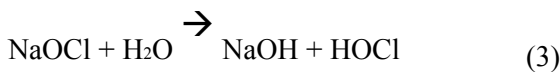
Color, pH, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS) and chlorides were measured using Standard Methods.

Color removal was measured for each dye at the wavelength in the visible range, where maximum absorbance was obtained. Residual hydrogen peroxide was determined by titrating against 0.1N Sodium Thiosulfate. Due to high concentration of chlorides present in sample because of using hypochlorite, sample was reacted with mercuric sulfate (HgSO_4) as 0.2gm per 20mL of sample, before measuring COD.

3. RESULTS AND DISCUSSIONS

3.1. Effect of Sodium Hypochlorite

When NaOCl dissolves in water, it dissociates into caustic soda (NaOH) and hypochlorous acid (HOCl), as shown in eq. 3 (Douglas G. Kelley, 2004);



The addition of NaOH into the water drives the pH to more alkaline levels. Hypochlorous acid, is also called “free chlorine”. However, HOCl is a weak acid in water, meaning that it partially dissociates into the

hypochlorite anion (OCl^-), as shown in eq. 4 (Douglas G. Kelley, 2004);



Hypochlorous acid is a strong oxidant (1.49V) and OCl^- is a weaker oxidant (0.94V). There is always an active equilibrium going on in water as chlorine switches back and forth from HOCl form to the OCl^- form. At a pH of 7.5, 50% of the chlorine in the water will be in the HOCl form and 50% will be in the OCl^- form.

Thus at an effective dose, NaOCl provides perfect combination of both oxidants and ultimately helps in both color removal as shown in fig. 2 and COD reduction. At higher concentration of hypochlorite, color reduction is fast but COD reduction takes time. Moreover, with the increase in hypochlorite concentration, it had led to increase in TDS level because of the formation NaCl in the reactor. It was found that 1.5g/L of sodium hypochlorite was appropriate for the sample.

3.2. Effect of Fe^{2+} dose

Iron in Hydrogen peroxide initiated reactions acts as an activator and helps in generating OH^\cdot radical.

These radicals then degrades the toxic compounds to simpler compounds as it is a strong oxidant. Iron dose also helps in color reduction and COD reduction. The sample was tested at different concentrations of Fe^{2+} , i.e. 0.084g/L, 0.1684g/L, 0.3368g/L, which was taken from the stock solution initially prepared and found that, the treated sample showed color change indicating that color removal could be achieved at low concentration of Fe^{2+} as shown in fig. 2. Studies have shown that during Fenton’s oxidation, color removal was faster than COD removal (Kang and Chang, 1997). The reason could be due to the formation of stable intermediate products, which require longer time for further oxidation.

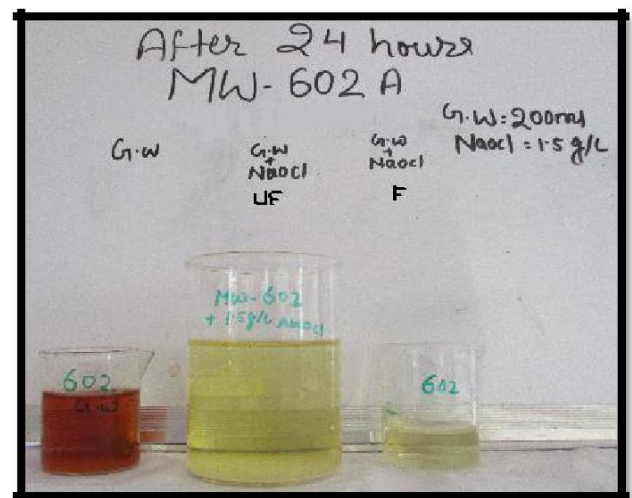


FIG. 1: Color change with sodium hypochlorite

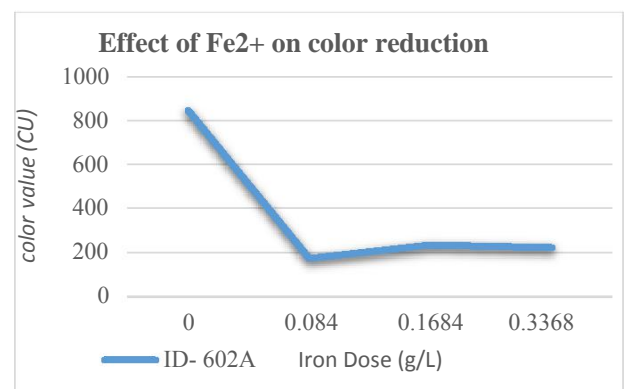


FIG. 2: Effect of Fe^{2+} on color reduction at different dose

3.3. Effect of H_2O_2 dose

It is known that addition of H_2O_2 influences the decomposition of complex organic compounds by Fenton’s reaction. Though, addition of only H_2O_2 did not resulted in significant change in color and COD. So, it was combined with NaOCl to enhance treatment.

Different concentrations of H₂O₂ were tested at 0.25g/L, 0.5g/L and 0.75g/L with NaOCl concentration fixed at 1.5g/L along with iron dose. Each concentration showed a half- life time of 24 hours which can be easily used for injecting in sub-surface.

As the concentration of H₂O₂ increased, COD reduced. Further increase in the concentration does not enhanced the treatment. With all these combination, COD removal was maximum with 0.75g/L concentration of H₂O₂ but color removal was not significant at this concentration. So, 0.5g/L of H₂O₂ concentration with 1.5g/L of NaOCl was again tested and showed about 78% of COD reduction 93% of color reduction and about 50% TDS removal as shown in Fig. 4. In order to remove color imparted by Fe²⁺, NaOH was added so that it converts to Fe³⁺ and precipitates out removing the color also. So, the sample became clear as shown in fig.3.

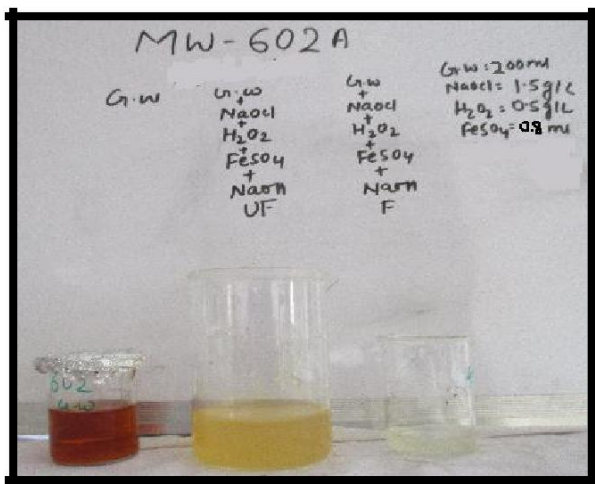


FIG. 3: Color removal after treatment

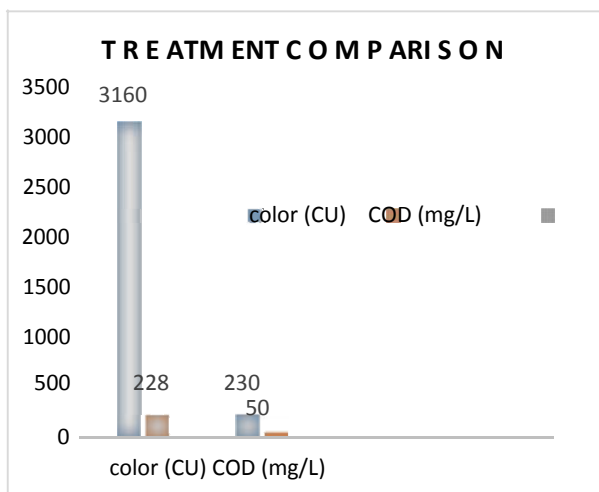


FIG. NO.4: Comparison of characteristics before and after treatment

4. CONCLUSION

ISCO is gaining increased popularity for site clean-up. Hydrogen peroxide based CHP has near-universal reactivity with all sorbed and soluble organic contaminants. The present study showed that catalysed hydrogen peroxide can be effective to decolorize and demineralize the groundwater and used as site remediation. The experimental results indicate that during Fenton's oxidation, decolourization was faster than degradation. The rate of oxidation was influenced by dose of Fe²⁺, H₂O₂, and sodium Hypochlorite. The optimum conditions required for maximum degradation were 1.5g/L of sodium hypochlorite, 0.5g/L of H₂O₂ and accordingly Fe²⁺ dose. Fe²⁺ added is 5-25 parts wt/wt to hydrogen peroxide. This investigation has demonstrated the potential of applying Fenton's process for the treatment of groundwater.

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