Advanced Oxidation Process (AOP) for Removing High Concentration of Iron in Drinking Water Sources

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Abstract: Iron can be removed from drinking water by advanced oxidation process (AOP) especially when the concentration of the metal is high and variable. The study focusses on the oxidation of iron using UV lamp of 8 watts and H_2O_2 in 1:1 proportion with the iron concentration present in water. Operating parameters investigated are iron concentration and reaction time. Experiments were conducted with tap water spiked with iron concentrations from 0.3 -10 mg/l. The results shows that iron can be brought down to the IS limits using AOP, provided proper contact time is given. For concentrations of range 0.3-1, 1-5 and 5-10 mg/l, the time required for attaining the permissible limits prescribed by IS 10500 2012 is 30 minutes, 90 minutes and 180 minutes respectively. This study reveals that AOP is an efficient method that can be adopted for treating water high in iron and to bring down its concentration to potable limits.

Keywords: Drinking water, Iron, Advanced Oxidation, H_2O_2, UV lamp.
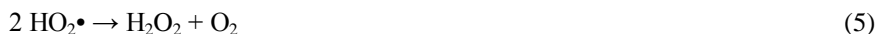
Introduction

Iron can be a troublesome chemical in drinking water. Rainwater, as it infiltrates the soil and underlying geologic formations, dissolves iron, causing it to seep into aquifers that serve as sources of groundwater for wells. In drinking water, iron is seldom found at concentrations greater than 10 mg/l. However, as little as 0.3 mg/l can cause water to turn a reddish brown colour. Iron is mainly present in water in two forms: either the soluble ferrous iron or the insoluble ferric iron. Water containing ferrous iron is clear and colour less because, iron is completely dissolved. When exposed to air, the water turns cloudy and a reddish brown substance begins to form. This sediment is the oxidized or ferric form of iron that will not dissolve in water.

Iron has become an important water pollutant now a days. Oxidation, aeration, ion exchange etc are some of the common methods adopted for the removal of iron from water. Ion exchange involves the use of synthetic resins, dolomite coated manganese dioxide [1] or other similar materials, where an ion on the solid phase is exchanged for the unwanted ions in the water [2]. Ion exchange method is effective for iron removal but it releases sodium ions which increase its concentration in treated water. So it is not a practical water treatment option for those who are concerned with sodium intake. Also, this process is not effective on organic iron. Polyphosphate treatment is limited to low levels of contamination up to 1 mg/l. At this level the dissolved iron is stabilized and dispersed, and cannot react with the oxygen. Since the metals are not removed, odour and taste of the iron remain in the water. Phosphate compounds are not stable at high temperatures. If the water is boiled it becomes destabilized and iron will come out of solution. High levels of dissolved iron concentration, up to 5 mg/l, can be treated with aeration followed by filtration. Aeration mixes oxygen rich air with treated water and converts soluble iron into insoluble form [3]. Oxidation is the most effective method for the removal of iron from water. It oxidizes soluble ferrous in to ferric form and it gets precipitated out. It can be easily removed from water by giving filtration as a post treatment. Oxidants like potassium permanganate [4], sodium hypochlorate [5] hydrogen peroxide etc. can be used. Oxygen can be injected by air bubbling other than adding a chemical oxidant [6]. The methods like ultracentrifugation [7] adsorption in granular activated carbon [8] has been already investigated for the removal of iron from water. Using ultracentrifugation 76% of iron was removed with an influent concentration of 10 mg/l. Biological methods of metal recovery termed as biosorption have been suggested as a cheaper, more effective alternative to existing treatment techniques. The process of adsorption is a well-established and powerful technique for treating domestic and industrial effluent. In this method a low cost adsorbent, generally an agricultural waste is used [9]. Different forms of inexpensive, plant materials such as Bengal gram husk [9], rice husk [10], sugarcane baggase [10, 11], reed mace [12], coconut shell charcoal [13], brown sea weed [14], coconut coir [11], bamboo charcoals [15], water hyacinth [16] have been widely investigated as a potential biosorbents for iron. A removal efficiency of 70% was obtained with an influent iron concentration of 100 mg/l using Bengal gram husk. The above mentionesd conventional methods may not be able to meet the current IS standards when the amount of iron is in the

effluent is very high. So the need for developing an efficient method for the removal of iron has become necessary in the present scenario.

Advanced oxidation process (AOP) comprises a range of similar but different chemical processes aimed at tackling pollution in water, air and soil [17]. The term advanced oxidation refers specifically to processes in which oxidation of contaminants occurs primarily through reactions with hydroxyl radicals. In water treatment applications, AOPs usually refer to a specific subset of processes that involve O_3, Fe^{2+}, H_2O_2, and/or UV light. It can be used for the removal of both organic and inorganic pollutants. Iron based sulphite photo oxidation process can be used for the removal of arsenic [18]. O_3, O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, Fe_2/H_2O_2 can be used for chemical oxygen demand (COD), colour and pesticide removal [19, 20, 21, 22]. Advanced oxidation process (AOPs) involve the two stages of oxidation: 1) the formation of strong oxidants (e.g., hydroxyl radicals) and 2) the reaction of these oxidants with organic and inorganic contaminants in water. These hydroxide ions are an efficient oxidizing agent which can also oxidize iron at higher oxidation rate. Thus iron can be converted into ferric hydroxides which can be precipitated out.

Among the various methods Hydrogen peroxide/UV light process is having low cost and H_2O_2 is a common oxidizing agent. This process includes H_2O_2 injection and mixing followed by a reactor that is equipped with UV light. During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. The reactions describing UV/H_2O_2 process are presented below

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet \tag{1}$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \tag{2}$$

$$H_2O_2 + HO_2\bullet \rightarrow HO\bullet + H_2O + O_2 \tag{3}$$

$$2\ HO\bullet \rightarrow H_2O_2 \tag{4}$$

$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{5}$$

$$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2 \tag{6}$$

In the aforementioned equations, Eq. 1 is the rate limiting reaction. Theoretically in UV/H_2O_2 process, the higher initial hydrogen peroxide concentration produces higher hydroxyl radical concentration (Eq. 1), which decomposes more target compound. However, an optimal hydrogen peroxide concentration exists because over dosing of hydrogen peroxide would lead to reaction with hydroxyl radical and formation of $HO_2\bullet$ (Eq. 2). UV/H_2O_2 process is efficient in mineralizing organic pollutants. A disadvantage of this process is that it cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum. Moreover, H_2O_2 has poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, then most of the light input to the reactor will be wasted. The major factors affecting this process are the initial concentration of the target compound, the amount of H_2O_2 used, wastewater pH, presence of bicarbonate and reaction time. UV/H_2O_2 process has been widely used for dyes removal. The combined use of UV/H_2O_2 with ultrasonic waves (US) has also been reported in order to enhance colour removal during dyeing wastewater treatment [21].

The main objective of the present study was to examine the feasibility of UV/ H_2O_2 advanced oxidation process in treating water contaminated by iron. The effects of reaction time and influent iron concentration were examined.

Materials and methods

Water sample preparation
The water samples used throughout the study were prepared from the stock iron solution with an iron content of 0.2 mg/ml using ferrous ammonium sulphate $(NH_4)_2Fe\ (SO_4)_2\cdot6H_2O$ and 1N potassium permanganate. The required amount of stock solution was mixed with tap water to get the iron concentrations of three ranges 0.3-1, 1-5 and 5-10 mg/l. The initial physico chemical characteristics of the tap water before spiking are shown in table 1. Experiments were done at 3 ranges of iron content. 1000 ml of sample prepared was adopted for the batch study.

Experimental setup
The experiments were carried out in a reactor of dimensions   30x25x15 cm. The AOP were designed to test the influence of operating parameters such as influent iron concentration (0.3- 10 mg/l) and treatment time. The pH was adjusted to neutral as the water was intended for drinking. It was adjusted using either 1M NaOH or 1M HNO_3. Hydrogen peroxide dosing was done in the ratio 1:1 with the iron concentration. 30% H_2O_2 was adopted and it was diluted to get the required amount. Mixing

Table 1. Influent water characteristics

Parameter	Value
Hardness	264 mg/l
pH	6.4
Residual chlorine	0 mg/l
Chloride	7.9 mg/l
Dissolved oxygen	5 mg/l
Iron	BDL*
TDS	54.2 mg/l
Alkalinity	16 mg/l

*before spiking with stock solution of iron

was done by a magnetic stirrer at 450 rpm. UV lamp of 8 watt capacity was adopted and it was kept at the top of the reactor in such a way that the entire radiation fell within the reactor. The samples were collected in half hour intervals and tested for iron content. The process was continued till it reached the permissible limit. The supernatant alone is taken for analysis of iron.
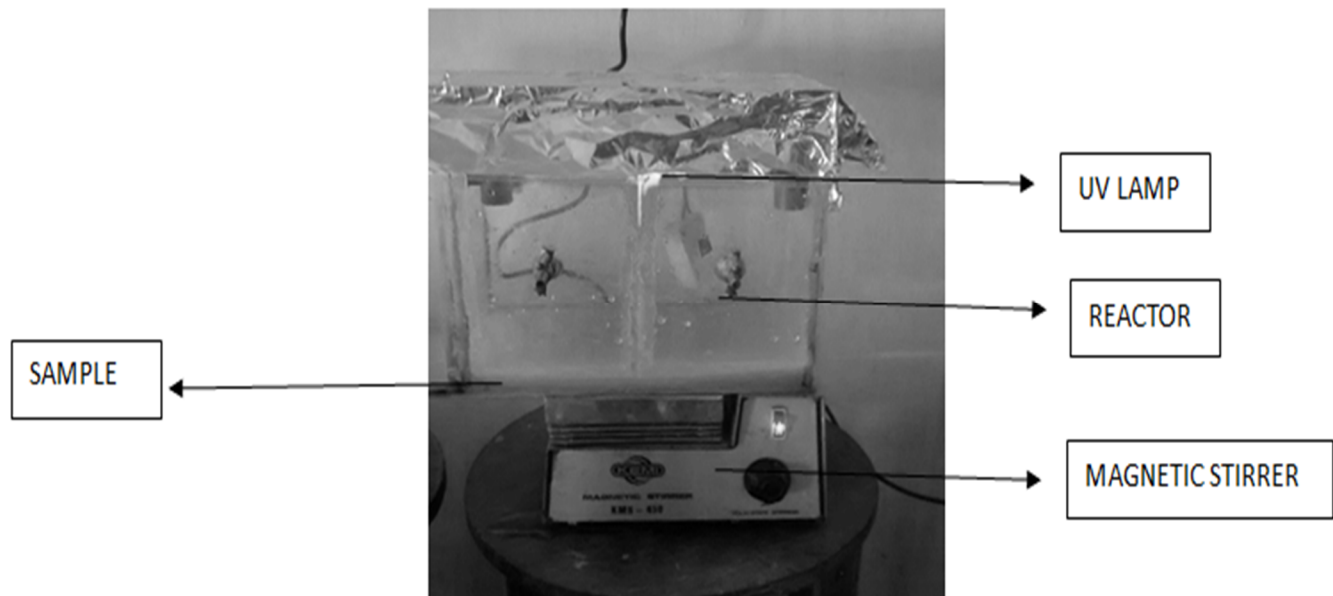

Figure 1. Experimental set up

Analytical techniques
Iron was measured by phenanthroline method as per APHA. Absorbance was measured using Systronics double beam spectrophotometer 2202 at 510 nanometer wavelength.

Results

The experiments were conducted until the residual concentration reached the IS 10500 2012 limits (0.3 mg/l). It indicates that higher the concentration of iron, the required time to achieve the IS limits is also higher. For 0.3 and 0.65 mg/l, the iron content reduced to 0.16 mg/l and 0.22 mg/l respectively after 30 minutes. But for 1 and 3 mg/l of iron content, the IS limits was reached only after 90 minutes and it has been reached up to 0.28 mg/l and 0.30 mg/l respectively. The effluent concentration reported for 5 mg/l was 0.12 mg/l after 120 minutes of reaction. Higher concentrations like 10 mg/l took 180 minutes to reduce the iron concentration to 0.25mg/l. A line of best fit was drawn with the values obtained after treatment and the co-efficient of determination was obtained as 0.88.

Table 2. Result of AOP

Influent iron concentration (mg/l)	Iron content at different time intervals (mg/l)					
	30 minutes	60 minutes	90 minutes	120 minutes	150 minutes	180 minutes
0.3	0.13	0.06				
0.65	0.22	0.09				
1.00	0.51	0.31	0.28			
3.00	1.2	0.61	0.30			
5.00	3.7	0.99	0.36	0.12		
10.00	6.89	3.37	1.59	0.69	0.49	0.25

Table 3. Summary of result

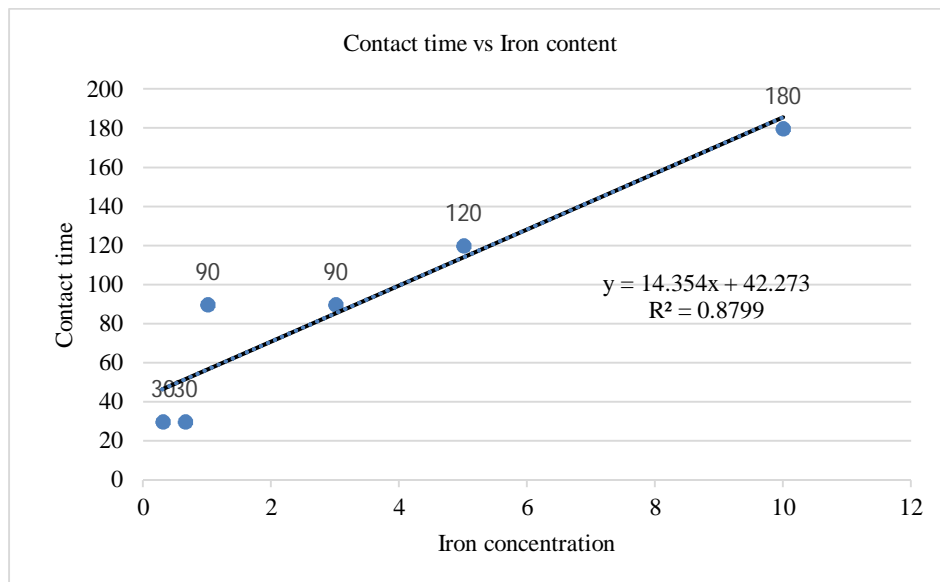| Influent iron concentration (mg/l)	Concentration of H_2O_2 (mg/l)	Time for achieving desirable/permissible limit as per IS 10500 2012 (Minutes)
0.3	0.3	30
0.65	0.65	30
1	1	90
3	3	90
5	5	120
10	10	180

Figure 2. Line of best fit

Conclusion

This study has shown the potential of advanced oxidation process for the removal of iron from contaminated water (influent concentration ranging from 0.3-10 mg/l) for potable purpose. Advanced oxidation process adopted was using UV and hydrogen peroxide. The pH was kept at neutral as treatment was intended for drinking purposes. It was seen that the contact time to reach the permissible limit increased with concentration of iron showing its significant effect on treatment. For a range of 0.3-10 mg/l of influent iron, the maximum time required for advanced oxidation to reduce the concentration to permissible limits is180 minute and for 0.3- 1 mg/l the maximum time obtained was 90 minutes. Coefficient of determination was obtained as 0.88. The study thus showed AOP as an effective method in treating influent water containing iron for a wide range of concentration often reported in drinking water sources.

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