OXIDATION OF SODIUM SULFIDE IN INDUSTRIAL WASTEWATER AND SPENT CAUSTIC BY HYDROCHLORITE ION SOLUTION

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Abstract: Oxidation of sulfide ion found in Ras Lanuf Oil and Gas Co (RasCo) industrial wastewater and spent caustic to soluble sulphate ion by hypochlorite ion. The method is based on industrial wastewater and spent caustic treatment with free dichromate ion hypochlorite ion solution for a short period of time sufficient to oxidize sulfide ion to sulphate ion. The method is practical and prompt to oxidize sulfide ion to sulphate ion.

Keywords: Industrial, Waste Water, Spent Caustic, Sulfide Ion, Oxidation, Hypochlorite Ion, Sulphate Ion Solution

INTRODUCTION

The extremely harmful sulfide found in industrial wastewater and spent caustic must be regulated to less than 1 mg S-2/L (Sulfide Treatment, 2010). The sources of sulfide are effluents of some petrochemical, refineries, chemical and tannery industries. Sulfides in industrial wastewater and spent caustic cause environment pollution as well air pollution via the formation and releasing of hydrogen sulfide (Saikat & Naveed, 2010; Saikat *et al*, 2010 and Ueno *et al*, 1979). In industrial wastewater and spent caustic sulfide, is converted by oxidation to thiosulfate, sulfite or sulfate, or it is removed from water by precipitation; in excess oxidants like hydrogen peroxide, chlorine, sodium hypochlorite and potassium permanganate sulfide ion is converted to sulfate ion (Allison *et al*, 2010; Kubicek, 2010 and Wanner *et al*, 2010). Sulfide is catalytically oxidized in spent caustic by air or hydrogen peroxide to thiosulfate or sulfate depends on the amount of oxidants (UOP, 2010). The aim of this work is to regulate the extremely nocuous sulfide ions in both RasCo's industrial wastewater and spent caustic to less than 1 mg S-2/L by oxidizing the nocuous sulfide ions to the innocuous sulfate ions in a short period of time by use dichromate free sodium hypochlorite solution.

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EXPERIMENTAL

Free dichromate alkaline sodium hypochlorite solutions having different hypochlorite ion content are tested to oxidize in a short period of time at room temperature. The harmful sulfide ion to the harmless sulfate ion in synthetic sulfide ion standard solutions and in seven spent caustic and industrial wastewater samples S1–S7. Sodium hypochlorite reacts with sodium sulfide according to the following chemical equation:

$$4NaOCl + Na_2S \rightarrow Na_2SO_4 + 4NaCl$$

Four synthetic standard alkaline sodium sulfide solutions containing 276, 250, 137 and 68 mg S-2/L are used. Standard alkaline sulfide ion solutions are prepared by weighing and dissolving sodium sulfide in distilled water to which a 2-3 mL 1M NaOH is added, followed by iodometric determination of the sulfide ion content in the synthetic alkaline standard solutions (Standard Methods for the Examination of Water and Wastewater 1985). The alkaline sodium sulfide solution pH is 12.80. Free dichromate sodium hypochlorite solution brought from RasCo's chlorination plant storage tank where it was produced from sea water electrolysis, it is used as received; sodium hypochlorite solution pH is 9.00. Hypochlorite ion concentration in the free dichromate sodium hypochlorite solution is determined iodometrically (Vogel 1972).

Experiment I

A 10.50 mL 1050 mg OCl-1/L alkaline sodium hypochlorite solution was added to a 50 mL 68 mg S-2/L alkaline sodium sulfide solution in an open 500 mL conical flask, the mixture was shaken manually at room temperature for about 2 minutes followed by iodometric determination of the excess non reacted sulfide ion in the same conical flask (Standard Methods for the Examination of Water and Wastewater, 1985).

Experiment II

In this experiment the sulfide ion concentration and volume as well the hypochlorite ion concentration are the same as in experiment I, but a 21 mL hypochlorite ion solution instead of 10.50 mL was added. The non reacted hypochlorite ion was determined iodometrically (Vogel, 1972). In both experiments I and II formation of sulfate ion was detected (Standard Methods for the Examination of Water and Wastewater, 1985).

Experiments I and II were repeated 13 times using different hypochlorite and sulfide ion concentrations, and applied to oxidize the sulfide ion in seven industrial wastewater and spent caustic samples S1 - S7 having sulfide ion concentrations 49, 53, 64, 62, 427, 450 and 464 mg S-2/L., samples pH is 10.60-13.60. The seven samples brought from RasCo's industrial wastewater treatment plant and ethylene plant. Table 1 tabulates concentrations and volumes of hypochlorite and sulfide ions mixed ratio in each experiment as well milligram hypochlorite ion added to each synthetic alkaline sulfide standard solution, industrial wastewater and spent caustic samples.

Table 1 hypochlorite and sulfide ions mixed ratio.

Experiment No.	mL S^{-2}	mg S^{-2}	mg S^{-2}/L	ml OCl^{-1}	mg OCl^{-1}	mg OCl^{-1}/L
1	50	3.40	68	10.50	11.03	1050
2	15	2.06	137	4	4.34	1084
3	20	2.74	137	6	6.50	1084
4	10	2.50	250	2	0.76	381
5	10	2.50	250	3	1.14	381
6	10	2.76	276	7	4.96	708
7	50	3.40	68	21	22.05	1050
8	15	2.06	137	10	10.84	1084
9	20	2.74	137	25	27.10	1084
10	40	5.48	137	25	27.10	1084
11	10	2.76	276	25	17.70	708
12	8	2.20	276	25	17.70	708
13	5	1.38	276	25	17.70	708
14	8	2.00	250	25	9.53	381
15	5	1.25	250	25	9.53	381
S1	150	7.35	49	25	23.15	926
S2	100	5.30	53	15	13.89	926
S3	20	1.28	64	10	9.26	926
S4	20	1.24	62	10	9.26	926
S5	10	4.27	427	25	23.15	926
S6	10	4.50	450	25	23.15	926
S7	10	4.64	464	25	23.15	926

RESULTS AND DISCUSSION

To observe and reveal the oxidation capability and potent immediate action of free dichromate hypochlorite ion upon sulfide ion; in experiments 1-6 the milligrams hypochlorite ion added to the synthetic alkaline sulfide ion standard solutions is less than the quantity needed to oxidize entirely the sulfide ion to sulfate ion. Furthermore, in experiments 7-15 the synthetic alkaline sulfide ion standard solutions, the industrial wastewater and spent caustic samples S1-S7 are treated with an appreciable amount of hypochlorite ion. That was to ensure the entire oxidation of the sulfide ion to sulfate ion as indicated by the iodometric methods results (Standard Methods for the Examination of Water and Wastewater, 1985 and Vogel, 1972). Table 2 tabulates milligrams reacted and milligrams non reacted of both hypochlorite and sulfide ions in each experiment and in industrial wastewater and spent caustic samples.

CONCLUSSION

Free dichromate hypochlorite ion solution regulates the concentration of sulfide ion to less than 1 mg S-2/L in both RasCo's industrial wastewater and spent caustic by oxidize at room temperature the extremely toxic sulfide ion to the nontoxic sulfate ion in a short period of time i.e. 2 minutes.

RECOMMENDATION

Ras Lanuf Oil & Gas Processing Co, petrochemical, chemical, refineries and tannery industries are recommended to use free dichromate alkaline sodium hypochlorite solution to oxidize the harmful sulfide ion in industrial wastewater and spent caustic to harmless sulfate ion.