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Ferrum Condition In Fenton and Ruff's Systems In The course of Indigo Carmine and Nitrophenol's Oxidation at Different pH Values.

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ABSTRACT

The influence of reaction mixtures' pH within the range 1 – 4.5 on oxidation process of indigo carmine and 3-nitrophenol using the systems of Ruff and Fenton was studied. It was demonstrated that in the course of both substrates' oxidation in reaction mixtures nano-sized particles of ferrum oxide hydrate are formed, the number of which depends on pH value. The value of [zeta]-potential gives evidence about interference of substrate molecules or intermediate oxidation products in agglomeration. Presence of agglomerates facilitates oxidation.

Keywords: Ruff's system, Fenton's system, ferrum oxide hydrate, nano-sized particles, indigo carmine, 3-nitrophenol.

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INTRODUCTION

Oxidative degradation as a means of water purification from organic pollutants is being an issue of a great interest. Ruff's and Fenton's systems, being basically hydrogen peroxide water solutions over ions of Fe^{3+} or Fe^{2+} respectively, are considered to be rather perspective oxidizers and they have been being investigated for quite a long time.

General notion about abovementioned oxidizing systems' action mechanisms is generation high-reactive hydrogen peroxide or hydroxide radicals from hydrogen peroxide, influenced by ferrum ions [1, 2]. According to [3, 4], oxidation of most organic compounds (colourants, phenols, organochlorine compounds) under action of Fenton and Ruff's chemical agents demonstrates the highest effectiveness when used at baseline pH values of 2,7-3,5. In this field predominant form of catalysts is represented by ions of $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})^{2+}$ [3]. When pH value is more than 3,5, hydroxide complexes Fe^{3+} that are forming have a tendency to polymerization, and oxidation of organic substances may be accompanied by persorption of baseline substrates, intermediate and final products of the reaction on polymer ferrum hydroxide complexes [3]. At pH > 4 concentration of catalyst's active form weakens owing to beginning of subsidence of ferrum hydroxide.

Currently the possibility of application of Ruff's and Fenton's systems for water purification from pollutants with low biodegradability is being intensively investigated [5 - 8]. A high percentage of these investigations study how conditions of substrates' oxidation influence on the process (baseline pH value, correlation of oxidizing agents etc.), as well as oxidizing degradation's trends and companion processes. However, the question regarding trends of ferrum ions' state changing in reaction systems, while substrate oxidation is still open.

Earlier, in the course of ethoxylate nolyphenol's oxidation with Ruff's and Fenton's systems (pH=3,0-5,0) by means of dynamic light scattering method, we managed to visualize formation of light-diffusing particles, which are ferrum hydroxide complexes [9]. Since the substrate being oxidized was a surface-active compound, the process was complicated by colloid-chemical effects. The concern was to see how far the trends determined were applicable to substances that do not have signified surface activity.

Indigo carmine and 3-nitrophenol were chosen as substrates for this work; possibility of indigo carmine's oxidation with Fenton's chemical agent is shown in [10, 11] and possibility of 3-nitrophenol's oxidation with Fenton's chemical agent is shown in [12].

METHODS

Indigo carmine and 3-nitrophenol of AR grade were used without additional purification.

The volume of reaction mixture was 25 ml, and substrate's baseline concentration was 70.3 $\mu\text{mol/l}$ for indigo carmine and 250 $\mu\text{mol/l}$ for 3-nitrophenol. Calculated amounts of hydrogen peroxide solution and ferric sulphate (II) solution were added to study mixture in case Fenton's system was used, or ferric chloride (III) solution in case Ruff's system was used, so that the baseline concentration of hydrogen peroxide at indigo carmine's oxidation was 0.34 $\mu\text{mol/l}$, while 3-nitrophenol was oxidized – 4 $\mu\text{mol/l}$, and ferrum ions in both cases – 25 $\mu\text{mol/l}$. Solutions were acidized with sulphuric acid.

pH values of reaction mixtures were traced with the help of pH indicator Mettler Toledo. Substrates' concentration changes were traced using spectrophotometry method with the help of spectrophotometer Solar CM2203, which allowed to thermostate the cuvette. Oxidation was performed at constant temperature of 25°C. Upon completion of oxidation, distribution of particles in solution was assessed by size by dynamic light scattering method, and their [zeta]-potential was determined with the help of ZetaSizer Nano ZS device.

MAIN PART

Results of indigo carmine and 3-nitrophenol's oxidation with both Ruff's and Fenton's systems with various pH values of reaction medium (see the Table) has been generally consistent with current knowledge about optimal pH interval (2,5-3,5). When pH = 4.5, significant lowering of 3-nitrophenol's conversion degree is observed, while oxidation of indigo carmine is still performed with high effectiveness.

Observed dependence of oxidation effectiveness from pH is compatible with current knowledge about defining role of ferrum in this process. However, study of reaction systems by means of dynamic light scattering method allowed recording a significant number of nano-sized particles in solution, which are of optimal pH interval. This means that not only hydroxoions, but also large agglomerates of ferrum oxide hydrate are present in the system. It seems that oxide hydrate's particles participate in oxidation process and favour its behavior. Indeed, nano-sized particles were identified in solutions with pH of 1 – 1.5, though, much fewer, as evidenced by the rate of curves of particles' distribution by size (wide curves with flat maximum). These solutions were characterized by much lower conversional degree compared with solutions with higher content of light-diffusing particles (see the Table).

It should be noted that in the absence of the substrates light-diffusing particles are also present in solutions and their number and diameter depend on pH value. Particles with a diameter of 60-260 nm were detected in Fenton's chemical agent yet in 2 hours after it had been prepared. In solutions of Ruff's chemical agents particles with a diameter of 10-120 nm were observed, besides, the size doesn't depend on oxidizing system.

On completing of oxidation of 3-nitrophenol with Fenton's system, in most solutions particles sized 40-100 nm were found. When this substrate was oxidized with Ruff's system, particles with a mean diameter of 100-800 nm were found. This may be conditioned by complex formation, accompanying the process of oxidizing degradation as a result of interreaction of Fe³⁺ ions with a substrate or intermediate products of its oxidation. Also, we can't rule out adsorption of the substrate and intermediates on the surface of ferrum hydroxide's particles.

Participation of substrate or intermediates in aggregation process is also testified by the results of determination of particles' [zeta]-potential, which stayed in solution upon completion of substrates' oxidation. In the absence of substrate at any pH values, the value of [zeta]-potential is positive (see the Table). In the presence of indigo carmine, charge of particles in many cases is reversed: in both Ruff's and Fenton's systems [zeta]-potential becomes negative hardly in all of studied pH range, being neutral in highly acid mediums only (see the Table). When 3-nitrophenol is oxidized, negative [zeta]-potential was observed in one test only (Ruff's system, pH=4.5). All other conditions were characterized by formation of particles with weak positive or neutral value of [zeta]-potential (see the Table). It seems that 3-nitrophenol and intermediate products of its degradation influence aggregation of iron-containing particles to much lesser extent than indigo carmine and intermediate products of its degradation.

Table: Degree of conversion of substrates and values of [zeta]-potential in solution on completion of oxidation.

Oxidizing chemical agent	pH	Substrate				In the absence of a substrate [zeta], mV
		Indigo carmine		3-nitrophenol		
		Degree of conversion, %	[zeta], mV	Degree of conversion, %	[zeta], mV	
Ruff's system	4,5	99	-17	45	-14	25
	3,5	100	-15	85	2	5
	2,5	100	-3	86	5	3
	1,5	56	-2	27	-	3
	1	15	Not detected	0	-	2
Fenton's system	4,5	100	-20	82	0	12
	3,5	100	-15	85	3	6
	2,5	100	-3	87	3	3
	1,5	77	0	59	3	5
	1	52	0	6	2	2

SUMMARY

As can be seen from the above, in the process of indigo carmine and 3-nitrophenole's oxidation nano-sized particles are detected in reaction mixture at a wide range of pH values, even at rather low values, though at pH =1-1,5 the amount of such particles is low.

CONCLUSION

The process of oxidizing degradation proceeds not in homogeneous, but in microheterogeneous medium, at this, aggregation process proceeds with participation of a substrate or intermediate products of its oxidation. Agglomerates of ferric oxide hydrate in studied pH interval facilitate the process of substrate oxidation.

It was stated that the presence of substrate is not a critical parameter of ferrum aggregates' formation, though the substrate, intermediates and intermediate products of its oxidation directly influence aggregates' characteristics (size and [zeta]-potential of the particles), which is probably conditioned by adsorption of oxidation products on particles' surface.

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