Photolytic AND Catalytic Destruction of Organic Waste Water Pollutants

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Abstract. The system: water supply source – potable and industrial water – wastewater – sewage treatment – water supply source is necessary for water supply and efficient utilization of water resources. Up-to-date technologies of waste water biological treatment require for special microorganisms, which are technologically complex and expensive but unable to solve all the problems. Application of photolytic and catalytically-oxidizing destruction is quite promising. However, the most reagents are strong oxidizers in catalytic oxidation of organic substances and can initiate toxic substance generation. Methodic and scientific approaches to assess bread making industry influence on the environment have been developed in this paper in order to support forecasting and taking technological decisions concerning reduction of this influence. Destructive methods have been tested: ultra violet irradiation and catalytic oxidation for extraction of organic compounds from waste water by natural reagents.

Introduction
Food industry always consumes a considerable amount of raw materials and energy, its waste water even exceeds raw materials and is removed from production departments as polluted water. Discharge of some pollutants into the atmosphere is considered hazardous. However, territorial inspecting authorities of consumer rights protection and human wellbeing do not control discharge into the atmosphere and waste water produced by many of these enterprises in Russia.

The paper is aimed at development of methodic and scientific approaches to assess influence of bread making industry on the environment, which supports forecasting and taking technological decisions to reduce this influence; as well as at testing destructive methods: ultraviolet irradiation and catalytic oxidation for extraction of organic compounds from waste water.

The paper has revealed key factors of anthropogenic impact on the environment of a bread making enterprise in Kemerovo region. Those include the sum total of internal (equipment, efficiency, fuel type, technology, assortment) and external (raw material quality) characteristics of the enterprise. Plus, equipment and technologies used in this enterprise are interrelating to amount and quality of pollution affecting eco-systems.

For example, for the manufacture of parts Dough as a constructive material used alloy steel X18H10T. It is important to note that when selecting steels in contact with food environment, it is
necessary to take into account their properties, operating conditions and design details of the nature of loads and stresses. Alloyed heat-treated steels have higher mechanical properties complex than carbon. They are better calcined possess higher strength and hardness. [1]

Pollutants emitted into the atmosphere by this enterprise have been detected in the following phases: delivery, storage and preparation of raw materials, dough making, baking, and transportation.[2] The analysis of data on emitted pollutants shows hazard “category” is made of delivery, storage, and raw material preparation (18.96%), dough making (0.02%), baking (60.65%), transportation (20.37%). Total value of specific discharge into the atmosphere over the complete technological cycle is given in Table 1.

| Table 1 - Specific discharge into the atmosphere |
|-----------------------------------------------|
|          | Solids, tons per year | Gaseous substances, tons per year |
| Ferric oxide | 0.124990           | Nitrogen dioxide | 2.816618 |
| Manganese | 0.002289            | Nitrogen oxide | 0.457525 |
| Black carbon (soot) | 12.425382         | Sulfurous anhydride | 2.701164 |
| Wood dust | 0.160000            | Carbon dioxide | 33.225803 |
| Flour dust | 0.330800           | Fluoric gaseous compounds | 0.000102 |

Waste water is mainly produced in the following phases: delivering and washing raw materials and equipment, and cooling system utilization. [3] Therefore, waste water is polluted generally by raw material remains, half-products, ready-made products and cleaning agents. These are complex polydisperse systems consisting of suspended particles, organic and mineral substances. [4,5] As far as we know, concentration of suspended particles in waste water of many bread making enterprises in Russia exceeds the mean industry standard (170 mg/l) and is three times higher than the permissible concentration for waste water (212 mg/l). BOD rate exceeds by 38% the mean industry standard (326 mg/l) and is 3.5 times higher than the permissible concentration for waste water (35.3 mg/l) [Orenburg].

Organic substances include: xylene, butanol, ethanol, acetic acid, formaldehyde, ethylene glycol etc. Table 2 presents their components in waste water of bread making enterprise, their hazard class and removal efficiency in conditions of decontaminated waste water discharge into the objects of household and general water consumption.

**Experiment**

Two groups of methods are applied for waste water treatment: regenerative and destructive ones. Regenerative methods make it possible to decontaminate waste water and extract organic substances and then use them. Destructive methods are applied if extraction of impurities from waste water is impossible or commercially useless. Main destructive methods of dissolved organic substances extraction from waste water include thermal-oxidation and oxidation.

Photolytic destruction of organic substances via ultraviolet irradiation [7] and catalytic oxidation was used for research into waste water treatment of a bread making enterprise. [12,13] Sample solution was made of components presented in Table 2; their concentration in waste water exceeded significantly the permissible concentration.
Table 2 - Organic substances in waste water of a bread making enterprise

| Pollutant       | Concentration in biological treatment, mg/l | Removable efficiency, % | LHI | Permissible concentration | Hazard class | Discharge, t/year | Discharge, mg/l |
|-----------------|---------------------------------------------|--------------------------|-----|---------------------------|--------------|------------------|-----------------|
| Xylene (xylol)  | 1.0                                        | 50                       | org.| 0.05                      | 3            | 0.188600         | 10.46           |
| Toluol          | 15                                         | 50                       | org.| 0.5                       | 4            | 0.080700         | 4.48            |
| Ethanol         | 14                                         | 70                       | general | -                         | -            | 3.305800         | 183.6           |
| Ethyl acetate   | -                                          | -                        | general | -                         | -            | 0.019200         | -               |
| Acetic acid     | -                                          | 80                       | org.| 1.0                       | 3            | 1.420000         | 78.89           |
| Nitrobenzene    | -                                          | 70                       | Standard | 0.2                      | 3            | 0.125000         | 13.61           |
| Formic acid     | -                                          | 85                       | BOD | -                         | -            | 0.146120         | 15.922          |
| Ethylene glycol | 1000                                        | 65                       | Standard | 1.0                      | 3            | 0.084560         | 9.177           |
| Formaldehyde    | 100                                         | 65                       | Standard | 0.05                     | 2            | 0.034560         | 3.76            |
| Petrol          |                                             |                          |      |                           |              | 0.040077         |                 |
| Kerosene        |                                             |                          |      |                           |              | 0.001278         |                 |

Ultraviolet irradiation was carried out by 36 watt power lamp (wavelength 185.6 nm). 20 mg/l (concentrated) hydrogen peroxide and titanium chloride TiCl$_3$ (at a rate of 0.2 g titanium per 1 liter water) were gradually injected beforehand into 1.5 liter reference water (sample solution). The solution was aerated by a bubbler. Table 3 presents the results of experiments.

Table 3 - Ultra violet destruction of organic substances in reference solution

| №   | Volume of solution, mg | H$_2$O$_2$. concentration g/l | Ti$^3+$ concentration mg/l | Chemical oxygen demand, mgO/dm$^3$ |
|-----|------------------------|-------------------------------|-----------------------------|-----------------------------------|
| 1   | 200                    | -                             | -                           | 886.8                             |
| 2   | 200                    | 10                            | 0.1                         | 547.3                             |
| 3   | 200                    | 20                            | 0.2                         | 408.3                             |
| 4   | 500                    | 30                            | 0.3                         | 463.6                             |
| 5   | 400                    | 40                            | 0.3                         | 450.2                             |

Organic compounds were also destructed as the result of catalytic oxidation. We used the system clay-hydrogen peroxide in our experiment. The results are provided in Table 4.

Table 4 - Catalytic oxidation of organic substances

| №   | Volume of solution, ml | H$_2$O$_2$. concentration ml | Clay, g | Chemical oxygen demand, mgO/dm$^3$ |
|-----|------------------------|------------------------------|---------|-----------------------------------|
|     |                        |                              |         | day | 3 days       | 5 days |
| 1   | 200                    | -                            | -       | 886.8 |              |        |
| 2   | 200                    | 4.0                          | 8.0     | 843.6 | 680.5        | 524.7  |
| 3   | 200                    | 6.0                          | 10.0    | 755.0 | 605.7        | 406.5  |
| 4   | 400                    | 10.0                         | 10.0    | 775.8 | 634.5        | 446.0  |
| 5   | 500                    | 10.0                         | 10.0    | 808.0 | 723.6        | 465.6  |
Discussion of results
As the result of ultraviolet irradiation oxygen dissolved in water transforms into ozone, which, in its
turn, can oxidize organic substances if an active catalyst – titanium hydro peroxide is in solution. And
the catalyst itself furthers decomposition of excessive hydrogen peroxide.
Presented in Table 4 results of investigation into destruction of organic substances under ultraviolet
irradiation demonstrate the optimal correlation of H2O2,mg/l and Ti3+mg/l concentrations,
conditioning nearly double decrease in chemical oxygen demand, is 20 mg/l H2O2 and 0.2 mg/l Ti3+.
It is known that chlorine, sodium hypochlorite, chlorine dioxide and other reagents are used to
obtain this correlation and can initiate generation of toxic substances. Fenton reagent (ferrum II
sulphate – hydrogen peroxide) is a quite efficient oxidizer used for removal of organic substances
from waste water [Fenton].
Clay is fine-dispersed according to its granulometric composition, and its chemical composition is
presented in Table 5.

| Clay               | SiO2   | Al2O3 | Fe2O3 | TiO2   | CaO   | MgO   | K2O   | Na2O | SO3 III |
|--------------------|--------|-------|-------|--------|-------|-------|-------|------|---------|
| Nizhe-Uvelsk deposit | 54.27-63.09 | 22.63-29.04 | 2.60-3.28 | 1.35-1.53 | 0.65-1.05 | 0.62-0.95 | 0.24-1.00 | 0.24-7.62 | 10.03 |

Ferrum III, aluminum, titanium in the chemical composition of clay in the system clay – hydrogen
peroxide facilitate processes of catalytic oxidation and coagulation [14]. Moreover, removal
efficiency of organic substances from waste water calculated in experiment according to chemical
oxygen demand (mg О/дм³) depended on the process duration and order of reagent injection into the
solution. If hydrogen peroxide was injected before clay, finally chemical oxygen demand was lower in
comparison with another succession.
The data in Table 5 on catalytic oxidation of organic substances by natural reagent – clay show
correlation 30mg/l H2O2, and 5% (mass) clay facilitates double reduction of chemical oxygen demand
over 5 days.

Conclusion
1. Complex methodological approach introduced in this paper to assess bread making industry
influence on the environment makes it possible to determine exposure degree of the enterprises on
nature and develop first-priority measures of control over technological processes. The latter are to
minimize anthropogenic impact at the most hazardous phases.
2. Intensification of in-receipt inspection of raw material quality can reduce pollutant formation.
3. Photolytic destruction of organic substances under ultraviolet irradiation and catalytic oxidation
favours waste water treatment and decrease in chemical oxygen demand.
4. Clay – a natural reagent used for oxidative and destructive treatment of waste water is an
efficient substance to shorten chemical oxygen demand in waste water without supplementary
preparation.

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