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ENVIRONMENTALLY FRIENDLY ADVANCED OXIDATION PROCESSES OF DYES BASED ON THE USE OF SOLID-PHASE OXIDIZING AGENTS

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Abstract. The main methods for removal dyes from wastewater and the essence of advanced oxidation processes are considered. The advantages of using solid-phase oxidizing agents compared to liquid-phase oxidants are presented. The influence of the specific power (P/V) of ultrasonic cavitation treatment on the efficiency and intensity of dyes degradation using advanced oxidation processes based on simultaneously activated by ultrasonic cavitation and catalysts of solid-phase oxidizing agents is analyzed. It was found that the degradation degree of Congo red using the advanced oxidation process "US/$FeSO_4$/PPI" at P/V=68 W/L was 97.2 %, and the degradation rate constant was 2.401×10^2 $M^{-1}s^{-1}$. It was also found that in the case of Rh B degradation using the advanced oxidation process "US/$MgMn_2O_4$/SPC" at P/V=51 W/L, the degradation degree was 98 %, and the rate constant was 0.308×10^2 $M^{-1}s^{-1}$. The expediency of applying the energy-saving principal when selecting the mode of US treatment is substantiated. A principal technological scheme for dyes degradation was developed, which included combined (cavitation and catalytic) activation of solid-phase oxidizing agents (PPI or SPC).

Keywords: advanced oxidation process, dye, ultrasonic cavitation, catalytic activation, solid-phase oxidizing agent, principal technological scheme.

1. Introduction

In the global industry, over 10 000 different dyes and pigments are used, and the annual worldwide production of synthetic dyes exceeds 700 000 tons (Zhou et al., 2019). It is known that about 200 000 tons of these dyes are lost with wastewater from the textile industry during dyeing and fabric processing operations (Ogugbue & Sawidis, 2011). According to the World Bank estimate, such wastewater makes up 17 to 20 % of the total volume of all industrial wastewater (Kant, 2012). Dyes, as components of aqueous media, can prevent the penetration of sunlight into the water column, suppress the photosynthesis of aquatic plants, and affect the reoxygenation and self-purification of water bodies, acting as a source of eutrophication (Bae et al., 2015; Mohod et al., 2023). Dye molecules in wastewater can also have carcinogenic and mutagenic effects, leading to dysfunctions of the liver, kidneys, reproductive, and central nervous systems in humans (Zhou et al., 2019).

The effectiveness of dye removal from wastewater using traditional processes (membrane filtration, adsorption, coagulation/flocculation) does not meet the requirements of The International Dye Industry Wastewater Discharge Quality Standards (Katheresan et al., 2018). These methods do not provide the mineralization of organic dyes (Ramana et al., 2022), and their use leads to the accumulation of precipitates or spent sorbents that require disposal. Biological methods of dye

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removal are characterized by significant disadvantages: the need to maintain optimal conditions for the degradation of pollutants (specific temperature values, pH of the reaction medium, required aeration mode) (Kumari & Kumar, 2023); they require large areas; and they are unsuitable for the removal of biologically stable dyes (Hayat et al., 2015).

Advanced oxidation processes (AOPs) are increasingly considered as highly competitive environmentally friendly water treatment technologies that can be used for the effective removal (mineralization) of organic pollutants with low biodegradability or high chemical stability (Al Mayyahi & Al-Asadi, 2018). The application limits of AOPs are defined by chemical oxygen demand (COD) values of ≤ 5 000 mg O_2/L (Kumari & Kumar, 2023). The essence of AOPs lies in the in situ generation of highly reactive species, primarily hydroxyl radicals ($^{\bullet}OH$) with an oxidation potential of 2.80 V (Tao, 2022). Hydroxyl radicals can rapidly and non-selectively attack stable organic compounds (Djeghader et al., 2023), particularly dyes, through hydrogen abstraction, electron transfer, and the development of radical processes (Zhang et al., 2021). The rate constants values for reactions between hydroxyl radicals and various organic compounds range from 10^6 to 10^9 $M^{-1}s^{-1}$ (Tao, 2022). The short life time of hydroxyl radicals in water (a few nanoseconds) causes their easy self-removal from the reaction system (Zhang et al., 2021). Other reactive oxygen species (ROS) that can be formed in various AOPs are superoxide radical anions ($O_2^{\bullet-}$), hydroperoxyl radicals ($HO_2^{\bullet}$), singlet oxygen ($^1O_2$), sulfate ($SO_4^{\bullet-}$), and carbonate ($CO_3^{\bullet-}$) radicals (Kumari & Kumar, 2023; Hübner et al., 2024).

Usually, liquid hydrogen peroxide is used as a source for generating free radicals, which is activated catalytically or by external energy inputs (Kumari & Kumar, 2023; Tao, 2022; Zhang et al., 2021; Hübner et al., 2024). However, aqueous solutions of hydrogen peroxide are thermally and chemically unstable, requiring significant economic costs for transportation and storage. Therefore, the modern trend in AOPs is the use of solid-form oxidizing agents (Sukhatskiy et al., 2024) such as periodates, sodium percarbonate, etc. These agents are much easier and cheaper to transport and store. As a result of their activation, a complex of ROS is generated, allowing for increased efficiency and intensity of the oxidative degradation of organic pollutants in aqueous media (Sukhatskiy et al., 2022). In chemical technology and ecology, there is currently a stable tendency toward integrating various processes. For example, the activation of hydrogen peroxide for the increased hydroxyl radicals generation is carried out simultaneously (synchronously) by iron (II) salts and ultrasound – the sono-Fenton process (Kumari & Kumar, 2023; Tao, 2022).

The aim of the work was to study the influence of the specific power of ultrasonic cavitation treatment on the efficiency and intensity of dyes degradation (Congo red/Rhodamine B) using AOPs based on catalyst-activated solid-phase oxidizing agents (potassium periodate or sodium percarbonate, respectively), as well as to develop a principal technological scheme of AOPs involving these agents.

2. Experimental part

Aqueous solutions of dyes – diazo dye (Congo red; CR) and xanthene dye (Rhodamine B; Rh B) – were prepared using distilled water with constant stirring on a magnetic stirrer. Two AOPs were developed for dyes degradation, in which solid-phase oxidizing agents (potassium periodate – PPI; sodium percarbonate – SPC) were synchronously activated by ultrasound (US) and a catalyst (ferrous sulfate or $MgMn_2O_4$ spinel nanoparticles, respectively). Thus, the "US/$FeSO_4$/PPI" process was applied for the degradation of CR, while the "US/$MgMn_2O_4$/SPC" process was used for the degradation of Rh B. $MgMn_2O_4$ spinel nanoparticles were synthesized by a co-precipitation method in a US field from aqueous precursor solutions ($Mg(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$, taken in a stoichiometric ratio of 1:2) with the addition of a precipitating agent – an aqueous sodium hydroxide solution with a concentration of 2 mol/L. The average crystallite size of $MgMn_2O_4$ (calcination temperature – 200 °C), calculated using the Debye-Scherrer equation based on X-ray diffraction results, was 24 nm. All other reagents were of analytical grade and purchased from Merck (Germany).

Experimental studies on dyes degradation were carried out in a thermostated glass reactor with a volume of 300 mL. The degradation was initiated by sequentially adding the solid-phase oxidant and the oxidant decomposition catalyst to the dye solution to intensify the generation of ROS. Simultaneously with the addition of the catalyst to the reaction medium, the US generator (frequency 22 kHz) was turned on – a magnetostrictive emitter "Ultrasonic Disintegrator" UD-20 (Poland), equipped with a panel for realizing the possibility of changing the specific power of cavitation treatment. The pH value of the reaction medium was adjusted using an aqueous solution of hydrochloric acid with a concentration of 0.1 mol/L.

The concentration of dyes in the reaction medium at a certain point in time was determined by UV-Vis spectroscopy method (UV-3100PC spectrophotometer;

China) at a wavelength of 574 nm (for CR) or 554 nm (for Rh B). At the same time, to separate the catalyst from the liquid phase, which was then analyzed for dyes content, the selected samples of the reaction medium were centrifuged for 5 min (frequency – 5 000 rpm). The effectiveness of dyes degradation using the developed AOPs was evaluated by the value of the degree of oxidative degradation (x, %) (Sukhatskiy et al., 2022), and the intensity was evaluated by the degradation rate constant.

3. Results and Discussion

An increase in the specific power of US cavitation treatment from 53.3 to 68.0 W/L (Fig. 1) significantly influenced the degree of CR degradation using the advanced oxidation process "US/$FeSO_4$/PPI": it increased by 21.5 % (from 75.7 to 97.2 %). This can be explained by the generation of a greater number of free radicals (particularly hydroxyl, iodyl, and periodyl radicals) with the increase in US power (Hamdaoui, Merouani, 2017) during the simultaneous activation of PPI by US and Fe^{2+} ions. However, further increasing the specific power to 83.3 W/L resulted in only a slight increase in the degradation degree to 98.2 %. In the case of a sharp increase in the concentration of generated ROS (hydroxyl, iodyl, and periodyl radicals) at higher US power, their recombination reactions begin to prevail over CR degradation (Sukhatskiy et al., 2022).

By constructing linear anamorphoses of kinetic curves in the coordinates of pseudo-first and second-order reactions, it was determined that the degradation of the CR diazo dye using the advanced oxidation process "US/$FeSO_4$/PPI" is most accurately described by the second-order reaction kinetic equation (see Table). A monotonic linear increase in the CR degradation rate constant with an increase in the specific power of US cavitation treatment was observed. This is consistent with the dependence of the Brilliant Blue R dye degradation rate constant using the "US/$NaIO_4$" process on US power (Hamdaoui & Merouani, 2017).

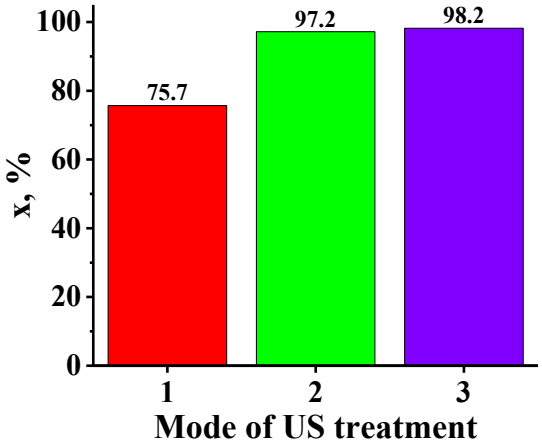

Fig. 1. The influence of different modes of US cavitation treatment on the degree of CR degradation using the advanced oxidation process "US/$FeSO_4$/PPI" (degradation conditions: the volume of the dye aqueous solution – 150 mL; C_0(CR) = 50 mg/L = 71.8 μM; the molar ratio of CR:$FeSO_4$:PPI = 1:5:10; the temperature – 20 °C; pH = 3.0; the degradation duration – 600 s). The specific power under different modes of US cavitation treatment, W/L: 1 – 53.3; 2 – 68.0; 3 – 83.3

Dependence of the rate constant of oxidative degradation of the CR diazo dye on the specific power of US cavitation treatment of the reaction medium

Specific power of US cavitation treatment, W/L	53.3	68.0	83.3
Pseudo-first order			
Rate constant $\times 10^2$, s^{-1}	0.613	0.907	1.245
Reliability of approximation (R^2)	0.934	0.807	0.791
Second order			
Rate constant $\times 10^{-2}$, $M^{-1}s^{-1}$	1.310	2.401	4.308
Reliability of approximation (R^2)	0.983	0.939	0.960

The dependencies of the degradation degree (Fig. 2) and the degradation rate constant of Rh B (Fig. 3) using the advanced oxidation process "US/$MgMn_2O_4$/SPC" on the specific power of US cavitation treatment had an extreme character with maximums (98 % and 0.308×10^2 $M^{-1}s^{-1}$, respectively) at 51 W/L. It was established that the degradation of Rh B, similarly to the degradation of CR, was most accurately described (R^2 = 0.973 at 51 W/L specific power) by the kinetic equation of the second-order reaction. In the case of using the kinetic equation of the pseudo-first order reaction – R^2 = 0.758.

An extreme character of the dependence of the values that characterizing the efficiency and intensity of Rh B degradation was due to the occurrence of a "choked cavitation" mode in the reaction medium at specific

power values exceeding 51 W/L (Patil et al., 2023; Šarc et al., 2017), that is, very small cavitation bubbles, which were easily subjected to coalescence. This significantly hindered the collapse of the formed bubble agglomerates, and therefore, the concentration of ROS involved in the oxidative degradation of Rh B decreased, which negatively influenced the degradation indicators and, accordingly, caused a deterioration in the ecological state of the aquatic environment. Similar results were obtained during studies on COD removal from greywater using the hybrid hydrodynamic cavitation + Fenton technique (Patil et al., 2023).

So, the rational values of specific power of US cavitation treatment for the degradation of CR using the advanced oxidation process "US/$FeSO_4$/PPI" and the degradation of Rh B using the process "US/$MgMn_2O_4$/SPC" were 68 and 51 W/L, respectively. Therefore, in practice, it is very important to be guided by the principle of saving energy resources when choosing the US treatment mode.

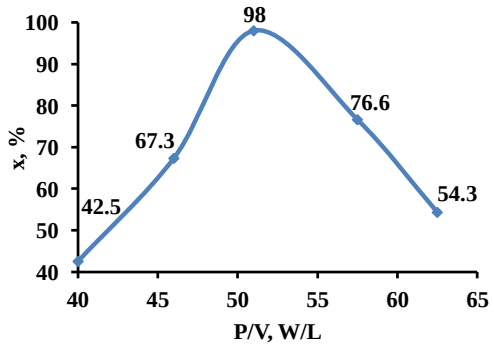

Fig. 2. The influence of the specific power of US cavitation treatment (P/V, W/L) on the degree of Rh B degradation (x, %) using the advanced oxidation process "US/$MgMn_2O_4$/SPC" (degradation conditions: C_0(Rh B) = 0.209 mM; C_0(SPC) = 5 mM; the catalyst dosage of 1.0 g/L; the temperature – 25 °C; pH = 3.0; the degradation duration – 3 600 s)

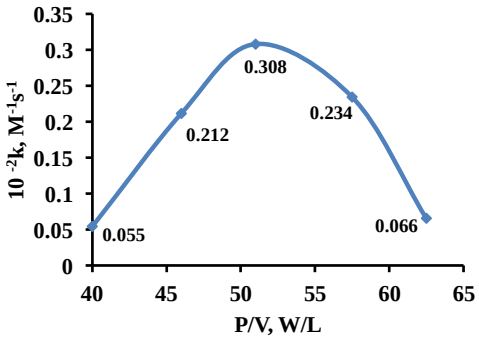

Fig. 3. The influence of the specific power of US cavitation treatment (P/V, W/L) on the degradation rate constant of Rh B (k, $M^{-1}s^{-1}$) using the advanced oxidation process "US/$MgMn_2O_4$/SPC" (degradation conditions: C_0(Rh B) = 0.209 mM; C_0(SPC) = 5 mM; the catalyst dosage of 1.0 g/L; the temperature – 25 °C; pH = 3.0; the degradation duration – 3 600 s)

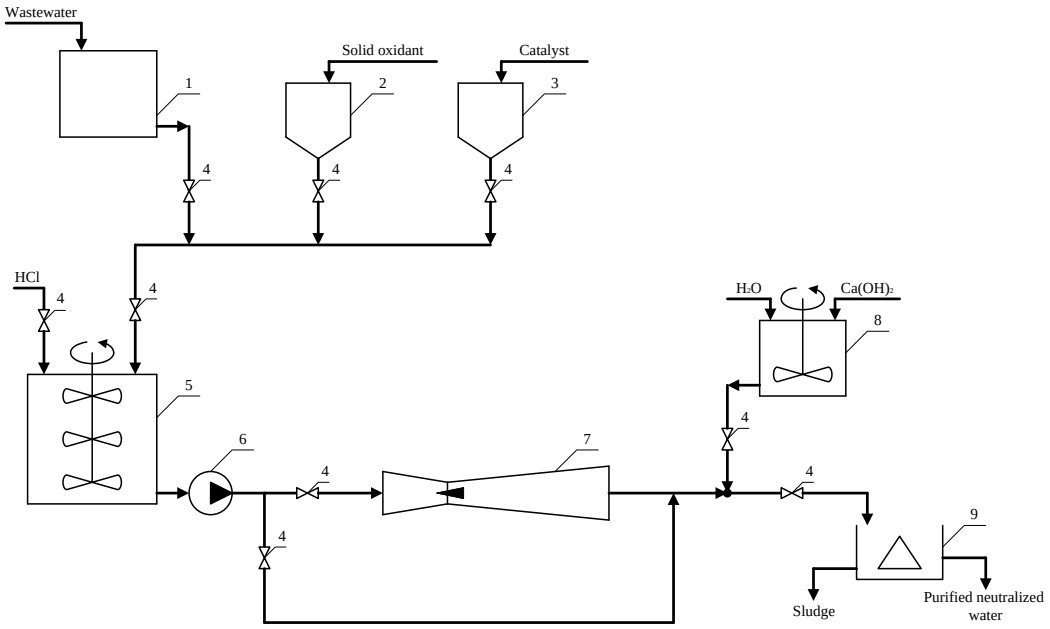

Fig. 4. A principal technological scheme of dyes degradation using AOPs based on cavitation- and catalyst-activated solid-phase oxidizers: 1 – averaging capacity; 2, 3 – bunkers; 4 – dispensers; 5, 8 – containers with a stirrer; 6 – pump; 7 – hydrodynamic jet cavitator; 9 – centrifuge

According to the results of experimental studies and considering the combined (cavitational and catalytic) activation of solid-phase oxidizing agents (PPI or SPC), a principal technological scheme for dyes degradation was proposed (Fig. 4). The key feature of this scheme is the use of a hydrodynamic jet cavitator for the realization of advanced processes of oxidative degradation of dyes on an industrial scale.

The scheme consists of three main units: 1) a unit for wastewater homogenization and reagent preparation; 2) a unit for combined (cavitation-catalytic) activation of the oxidizing agent and oxidative degradation of dyes; 3) a unit for neutralization of the aqueous medium and separation of sludges.

4. Conclusions

It was established that the degree of CR degradation using the advanced oxidation process "US/$FeSO_4$/PPI" at the specific power of US cavitation treatment of 68 W/L was 97.2 %, and the degradation rate constant was 2.401×10^2 $M^{-1}s^{-1}$. In the case of Rh B degradation using the advanced oxidation process "US/$MgMn_2O_4$/SPC" at the specific power of US cavitation treatment of 51 W/L, the degree of degradation was 98 %, and the rate constant was 0.308×10^2 $M^{-1}s^{-1}$. The feasibility of applying the principle of saving energy resources when choosing the mode of US treatment was justified. A principal technological scheme of dyes degradation was developed, which provided the use of a hydrodynamic jet cavitator for industrial scaling of environmentally friendly AOPs.

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