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Removal of Acid Red 27, Reactive Black 5 and Acid Green 16 from Aqueous Solutions using Potassium Ferrate(VI)

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Abstract

The article presents the possibility of using potassium ferrate(VI) (K_2FeO_4) to remove dyes (Acid Red 27, Reactive Black 5, Acid Green 16) belonging to the single azo, double azo and triarylmethane classes from aqueous solutions with an initial concentration of 100 mg/l (Chemical Oxygen Demand (COD) values for AR27, RB5 and AG16 sulutions were 172, 156 and 198 mg O_2/l, respectively). For the most favorable values of oxidation parameters of AR27 and RB5 (pH 7, K_2FeO_4 concentration, 180 and 240 mg/l, respectively, reaction time 10 min), visual discolouration of the aqueous solutions investigated and a decrease in COD values of 83.7% and 81.4%, respectively, were achieved. In the case of AG 16 dye, in the most favorable conditions of the oxidation process (pH 3, K_2FeO_4, concentration 300 mg/l, 15 min), visual discolouration and a decrease in the COD value of 83.8% were also obtained. The probable reasons for the higher resistance of AG16 to oxidation using K_2FeO_4 compared to AR27 and RB5 were also explained, based on the analysis of the structure and type of bonds present in the molecule AG 16.

Key words: *Acid Red 27, Reactive Black 5, Acid Green 16, potassium ferrate(VI), wastewater treatment, oxidation, dyes.*

Introduction

Dyes belong to one of the many organic substances, which, due to their wide industrial use, can get into the natural environment and contribute to adverse changes. Sewage containing dyes may come from various sources, in particular from the processes of their production and technological operations accompanying the production of textiles, such as dyeing and printing [1-4]. Most dyes are organic compounds with a complex chemical structure, characterised by some toxicity in relation to aquatic organisms, and their use in industry and, consequently, their presence in industrial wastewater is a significant problem, also due to their low biodegradability [5]. In some cases, dyes present in an aqueous environment may degrade under anaerobic conditions. Moreover, the degradation products may be found in the food chain and be toxic or carcinogenic to mammals [6-8]. In addition, due to the intense colour associated with the presence of dyes in the aquatic environment, there is a risk of significantly decreasing the penetration of sunlight into deeper layers of water, thus reducing oxygen absorption, which is necessary for the life of aquatic organisms [9]. Therefore, the use of properly effective wastewater treatment technologies containing dyes is necessary from the point of view of health, hygiene and environmental protection [10-11]. For this purpose, commonly known, often multi-stage, physicochemical methods of wastewater treatment are used. Application of these methods, although related to the removal of dyes, results in their significant concentration in emerging sediments, which is associated with difficulties in their development [12]. The use of potassium ferrate(VI) (K_2FeO_4) for this purpose is an advanced and appropriate approach to the treatment of this type of wastewater [13-15]. K_2FeO_4 contains an iron ion in the sixth oxidation state and is therefore characterised by strong oxidising properties, which is also associated with the value of its oxidation-reduction potential, which in an acidic environment is 2.2V, while in an alkaline environment $-$ 0.72V. In an aqueous environment Fe(VI) is reduced to Fe(III), which precipitates in the form of Fe(OH)$_3$. Therefore, K_2FeO_4 can act bi-directionally, i.e. as an oxidant in the first and as a coagulant in the second stage of the purification process. In addition, ions Fe^{3+} and H_2O are formed as a result of the degradation of in an acidic environment; therefore K_2FeO_4 was considered as a green chemical [13, 16-17]. This compound has also been used for the oxidation of dyes, such as azo dye Active Brilliant Red X-3B [18], azo dye Reactive Red 2BF [19], and xanthene dye Mordant Red 15 Dye [20]. The paper presents the results of the removal of three dyes belonging to azo dyes (single and double azo classes) and the triarylmethane class (Acid Red 27, Reactive Black 5, Acid Green 16) from aqueous solutions using K_2FeO_4. The aim of the research was to select
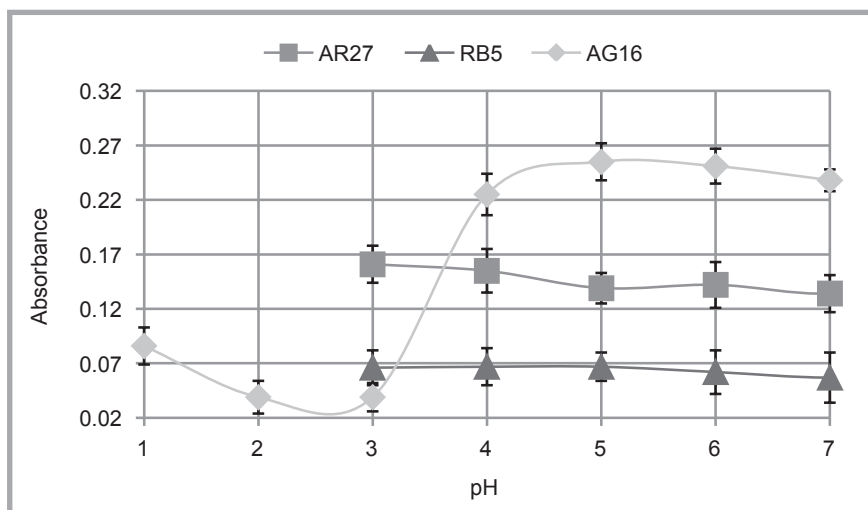
Figure 1. *Plot of absorbance values versus pH values for AR27, RB5 and AG16 solutions (concentration of dyes 100 mg/L, time 15 min, concentration of K_2FeO_4 200 mg/l).*
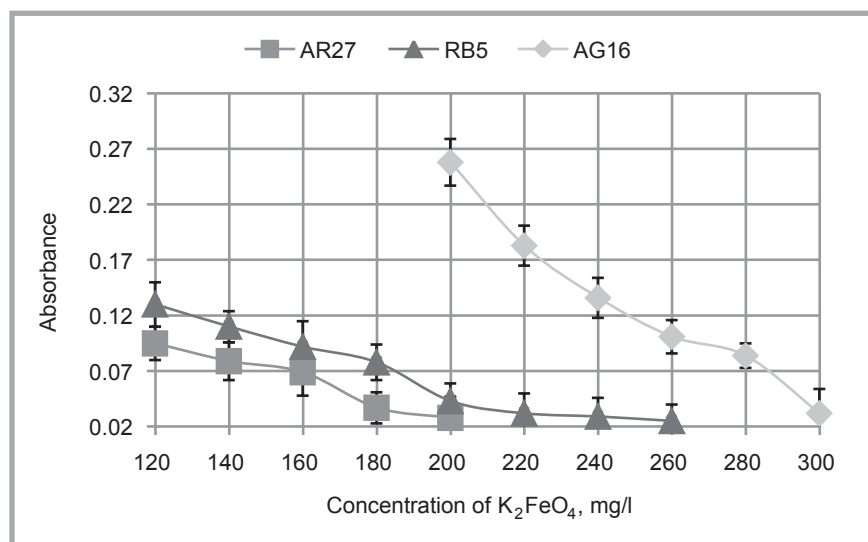
Figure 2. *Plot of absorbance values versus concentration of K_2FeO_4 values for AR27, RB5 and AG16 solutions (concentration of dyes 100 mg/l, time 15 min, pH 3 for AG16 and pH 7 for AR27 and RB5).*

an appropriate pH value of the reaction medium and K_2FeO_4 concentration for the dye solutions tested, after which the changes in the absorbance and COD values of the post-reaction solutions were determined for the most favorable values of these parameters for individual dyes in dependence on the reaction time.

Materials

During the tests, technical K_2FeO_4 (Envifer, Nano Iron, s.r.o., Czech Republic) containing 40.2% K_2FeO_4 (CAS 13718-66-6, 198.04 g/mol) was used. Dye solutions (100 mg/l) were prepared using distilled water and Acid Red 27 (AR 27, CAS 915-67-3, C.I. 16185, single azo class), Reactive Black 5 (RB5, CAS 12225-25-1, C.I. 20505, double azo

class) and Acid Green 16 (AG 16, CAS 3369-56-0, C.I. 44025, triarylmethane class). During the tests, a disproportionate dependence of the optical density (absorbance) on the concentration was not observed. Dyes were purchased from Boruta-Zachem S.A., Poland, and used without further purification. For pH correction, solutions of NaOH and H_2SO_4 at concentrations of 25%, analytical grade, were used.

Analytical methods

The pH value was determined using Inolab® pH/Ion/Cond 750 and a SenTix® 81 electrode (WTW, Germany) [21]. The maximum absorbance at 520 nm (AR27), 616 nm (RB5) and 640 nm (AG16) was determined using an SPE-

KOL-11 spectrophotometer (Carl Zeiss, Germany) after centrifuging the sample (4000 rpm, 5 min). The content of K_2FeO_4 in Envifer (by 505 nm) was determined using a UV-VIS spectrophotometer (Cary® 50 UV-VIS, Varian Inc., Australia) [22]. The COD value was determined by the standard dichromate method using sealed tubes and a PF-11 spectrophotometer (Macherey-Nagel, Germany) [23].

Conditions of experiments

The tests were carried out at a constant temperature of 19±1 °C in beakers containing 500 ml of the dye solutions tested, which were mixed with a magnetic stirrer (200 rpm, MS11, Wigo, Poland). To 500 ml of dye solution (AR27, RB5 or AG16) at a concentration of 100 mg/l, a specific amount (analitical balance, ±1 mg) was added. Envifer was calculated as pure K_2FeO_4, pH adjusted with 25% H_2SO_4 or NaOH solutions to the presumed value, and the reaction was carried out for a limited time. Immediately after the reaction completion, the sample was centrifuged, (4000 rpm, 5 min), the absorbance measured at the appropriate wavelength, and the COD assay was performed. The tests were carried out for pH in the range 1-7 using a constant dose of K_2FeO_4 (200 mg/l) for 15 min. In the next stage, tests were carried out for concentrations of K_2FeO_4 in the range of 120-300 mg/l for 15 min, assuming constant pH values of 3 (for AG 16) and pH 7 (for AR 27 and RB 5). For the most favorable pH and K_2FeO_4 concentration determined, the changes in absorbance values at appropriate wavelengths and COD were determined in dependence on the reaction time. As the main criteria for the effectiveness of the oxidation processes studied, the changes in the absorbance and COD values of the solutions analysed were adopted. All experiments were repeated three times.

Results and discussion

In the initial stage of the research, a quantitative analysis of a commercial product (Envifer) containing K_2FeO_4 was carried out. Determination of the K_2FeO_4 content was carried out using the spectrophotometric method, and the results obtained showed that Envifer contained 40.2% pure K_2FeO_4, which was adopted for calculating the doses of the technical product in the further part of the study. The dye solutions prepared

(AR27, RB5 and AG16) at a concentration of 100 mg/l were characterised by variable absorbance values (2.174, 2.440 and 2.168, respectively) and COD (172, 156 and 198 mg O_2/l, respectively). In order to select the appropriate pH value (*Figure 1*), tests were carried out in the 3-7 pH range for AR27 and RB5 and in the 1-7 pH range for AG16 at a constant dose of K_2FeO_4 of 200 mg/l over 15 min. In the case of AR27 and RB5, the lowest absorbance values and visual discolouration of the samples were obtained at pH 7 (0.134 and 0.057, respectively), while in the case of AG16, the pH was in the range of 2-3. On the basis of the tests conducted, pH 7 for AR27 and RB5 and pH 3 for AG16 were taken as the most advantageous, because the absorbance values obtained at pH 2 and 3 were comparable, and further acidification of the sample to pH 2 would not probably lead to higher dye removal efficiency. Other authors for azo dye Reactive Orange 16, obtained the highest efficiency of dye removal using K_2FeO_4 in a very alkaline (pH 10) and acidic (pH 2-3) environment [24]. In the next stage of the study, the concentration of K_2FeO_4 in the range of 120-300 mg/l was analysed (*Figure 2*). The tests were carried out at pH 7 for AR27 and RB5 and at pH 3 for AG16 for 15 min. The results obtained showed that for AR 27 the lowest values of absorbance were recorded after doses of K_2FeO_4 in the range of 180-200 mg/l, (0.037 and 0.028, respectively), with the difference in absorbance between doses being small – only 0.009. Therefore, for subsequent studies of AR27, 180 mg/l was the most favorable dose of K_2FeO_4. Achieving a significant decrease in the absorbance value for the RB5 dye required higher doses of K_2FeO_4, i.e. 240-260 mg/l, for which the absorbance values measured were 0.029 and 0.025, respectively.

For this dye, 240 mg/l was used as the most favorable dose of K_2FeO_4 for further testing. Thus, the AG16 oxidation process required the highest dose of K_2FeO_4, compared to those used for AR27 and RB5 (180 and 240 mg/l, respectively). In this case, the lowest absorbance value (0.032) was obtained for an K_2FeO_4 dose of 300 mg/l, which was taken as the most favourable for further tests. In the next stage, the dependence of the change in absorbance over time for individual dyes was investigated with an optimal pH value of 7 (for AR27 and RB5) and pH 3 (for AG16) and K_2FeO_4 dose of 180, 240 and 300 mg/l respec-
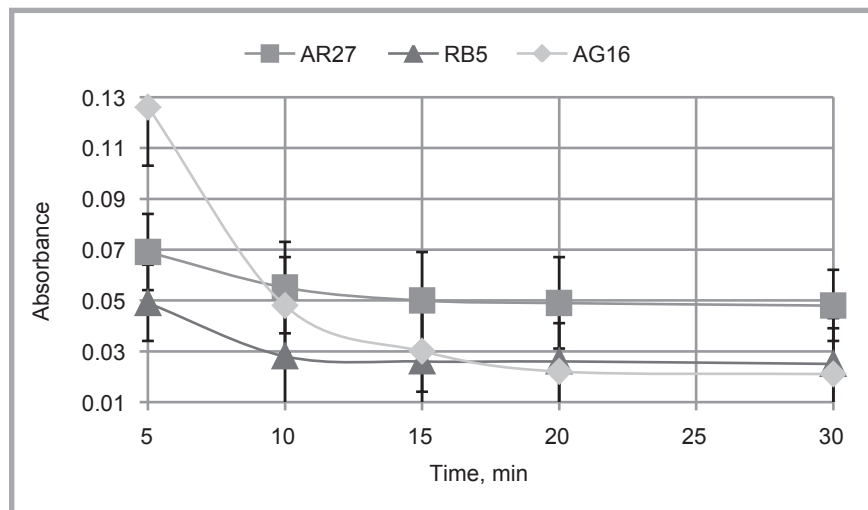

Figure 3. *Plot of absorbance values versus time values for AR27, RB5 and AG16 solutions (concentration of dyes 100 mg/l, pH 3 for AG16 and pH 7 for AR27 and RB5, concentration of K_2FeO_4 for AR27, RB5 and AG16: 180 mg/l, 240 mg/l and 300 mg/l, respectively).*
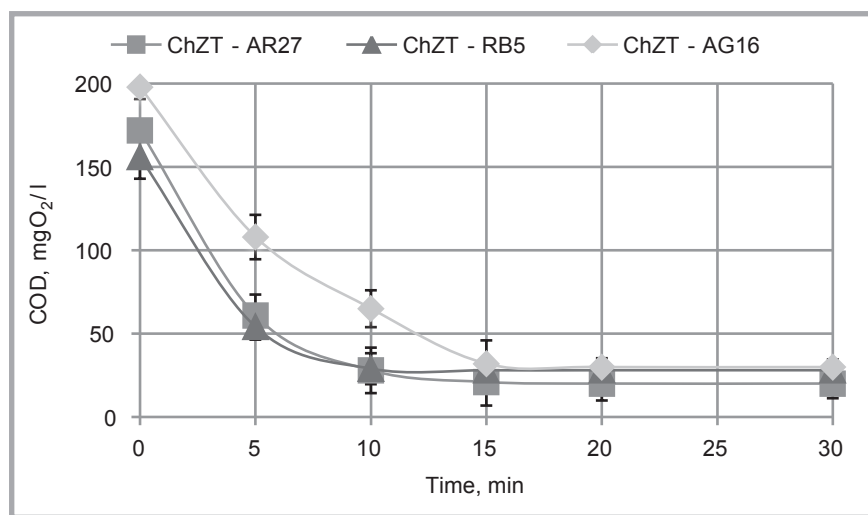

Figure 4. *Plot of COD values versus time values for AR27, RB5 and AG16 solutions (concentration of dyes 100 mg/l, pH 3 for AG16 and pH 7 for AR27 and RB5, concentration of K_2FeO_4 for AR27, RB5 and AG16: 180 mg/l, 240 mg/l and 300 mg/l, respectively).*

tively, at an initial dye concentration of 100 mg/l (*Figure 3*). The fastest decrease in the absorbance value was observed within 10 minutes of the process in the case of AR27 and RB5 (up to 0.055 and 0.028, respectively), where prolongation of the reaction time for these dyes did not significantly affect the exchange of absorbance. In the case of AR27, they changed in the range of 0.048-0.05, and in the case of RB5 – 0.022-0.026. After 10 minutes the duration of the process of the absorbance value was thus reduced by 97.5% for AR27 and 98.9% for RB5, respectively, in relation to the initial values. In the case of AG16, the largest changes in absorbance were recorded within a 15 minute duration of the process (absorbance value decreased to 0.03), after which it was subject to slight

changes in the range 0.025-0.026). After 15 minutes the decrease in the absorbance value was 98.6% compared to the initial value. Therefore, it was assumed that the effective removal of AR27 and RB5 from the aqueous solutions tested occurs after 10 minutes, while in the case of AG16, the duration of the process should be slightly longer – 15 minutes. In the next stage of the experiments, the dependence of changes in the COD value on time at pH 7 (for AR27 and RB5) and pH 3 (for AG16) and doses of K_2FeO_4, 180, 240 and 300 mg/l respectively, at an initial concentration of dyes of 100 mg/l was investigated (*Figure 4*). The research carried out showed that the most intense decrease in the COD value in relation to the initial values for AR27 and RB5 was recorded after 10 minutes

of reaction (83.7% and 81.4 %, respectively). The AG16 dye required a longer oxidation time (15 min.), in which case a reduction in the COD value of 83.8% was obtained. Further prolongation of the reaction time for all dyes did not significantly change the COD value of post-reaction solutions. Only changes in COD values in the range of 20-21 mg O_2/l were observed (for AR27). In the case of RB5 and AG16, the COD values determined for samples at subsequent measurement points were 28 and 30 mg O_2/l, respectively. A similar COD removal rate (73.3%) was reported for Reactive Red 2BF at an initial dye concentration of 100 mg/l, pH 4 and dose of K_2FeO_4 of 900 mg/l for 20 min [19]. When the Taguchi method was used to optimise the AG16 removal process from synthetic sewage at an initial concentration of AG16 20 mg/l, pH 2, concentration of K_2FeO_4 of 125 mg/l and reaction time of 50 min, the degree of dye removal was 98% [25]. The results obtained showed that oxidation conditions for dyes belonging to a similar class of organic compounds, i.e. the single and double azo classes (AR27 and RB5), require similar oxidation times, although in order to obtain comparable dye removal effects (*Figure 2*), the dose of K_2FeO_4 for RB5 should be slightly higher (240 mg/l). In the case of AG16, belonging to the triarylmethane class, it has been shown that it requires not only a longer oxidation time (15 min) and higher dose of K_2FeO_4 (300 mg/l) but also an acidic reaction medium (pH 3, in which the oxidizing effect of K_2FeO_4 is greater), as compared to AR27 and RB5. The results obtained indicate that AG16, belonging to the triarylmethane class, was characterised by greater resistance to oxidising K_2FeO_4 than AR27 and RB5, belonging to the single and double azo classes. Explanation of this fact is possible on the basis of an analysis of the structure of the AG16 molecule and the type of bonds present in AG16, subjected to oxidation reaction using K_2FeO_4. The molecules of triarylmethane dyes, including AG16, are characterised by the presence of a carbon-carbon double bond (–C=C–), for which the binding enthalpy value is 611 kJ/mol, in contrast to azo dyes, which are characterised by the presence of azo bonds (–N=N–), for which the binding enthalpy value is 456 kJ/mol. Research on the oxidation of green malachite, which is also a triarylmethane dye, similar to AG16, showed that first of all a hydrolytic attack takes place on the –C=C– bond, which is related to the creation of an imine quinone and benzoic acid. It wasalso proven that in addition to the –C=C– bond cleavage, N-dealkylation occurs, which results in degradation of the dye [26]. In the case of azo dyes, it was shown that during their oxidation, azo bonds do not rupture, but –C–N– bonds do, having a lower binding enthalpy value (306 kJ/mol) than azo bonds (456 kJ/mol). In this case, in the initial stage of oxidation, a hydrolytic attack on the –C–N– type bond occurs, resulting in diazo compounds and quinones. In the next stage of oxidation, diazo compounds are oxidised to phenol and molecular nitrogen, whereas quinones are oxidised to phthalic acid [27]. Therefore, AG16 showed greater resistance to oxidising K_2FeO_4, compared to AR27 and RB5, due to the presence in the molecule of other types of bonds and other mechanisms of degradation of the dye molecule. In the case of the AG16 oxidation processes, –C=C– bonds are broken, with a higher enthalpy thereof (611 kJ/mol), in contrast to the oxidation of AR27 and RB 5,, in the case of which the –C–N– bond is broken asthe binding is much lower, amounting to 306 kJ/mol.

◼ Conclusions

◼ The use of K_2FeO_4 for the oxidation of AR27, RB5 and AG16 was characterised by variable efficacy, with the most favorable conditions for the removal of AR27 and RB5 being at pH 7 and at an K_2FeO_4 concentration of 180 and 240 mg/l, respectively, within 10 min. Under these conditions, visual discolouration of the solution was obtained.

◼ In the case of AG16, the effective removal of the dye, resulting in visual discoloration of the aqueous solution, required the use of different oxidation conditions than in the case of AR27 and RB5 (pH 3, K_2FeO_4 concentration 300 mg/l, 15 min).

◼ The results of COD analyses in dependence on the reaction time, in the most favorable conditions of the oxidation process determined, showed that it is possible to reduce the COD value by 83.7% (AR27), 81.4% (RB5) and 83.8% (AG16) in relation to the initial values.

◼ The less susceptibility of AG16 to oxidation using K_2FeO_4, was caused by the necessity of breaking –C=C– bonds with a higher enthalpy value (611 kJ/mol), in contrast to AR27 and RB5 dyes, in the case of which –C–N– binding was broken, for which the enthalpy value is 306 kJ/mol.

◼ Based on the results obtained, it can be concluded that potassium ferrate(VI) is a promising and effective oxidant that can be successfully used for decolourising aqueous solutions and wastewater.

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