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Application of Spontaneous Oxidation Processes of Zero-valent Iron and Electrocoagulation for Reactive Black 5 Removal

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Abstract
Two methods of Reactive Black 5 dye removal were compared in this work, namely electrocoagulation (EC) and one based on spontaneous electrochemical oxidation of zero-valent iron (ZVI). Both methods are based on electrode processes and the sorption process and allow to achieve a similar effectiveness of dye removal. In the case of ZVI, however, a longer contact time or a greater surface area of the electrodes applied is necessary. In turn, the ZVI enables to conduct the processes of dye removal with no requirement for an external source of electric current (lower exploitation inputs). The study demonstrated that the application of both the ZVI method and EC is especially advisable in the case of lower initial concentrations of dye in the solution, i.e. the higher the concentration, the lower the contribution of electrode processes in dye removal from the solution and the greater the contribution of sorption processes.

Key words: *dye removal, zero-valent iron, electrocoagulation, reactive dyes.*

■ Introduction

Reactive dyes, like Reactive Black 5 (RB5), are highly applicable in the dyeing processes of final products. They are used in different industry branches, e.g. in the textile, plastics or leather industries. RB5 is a leading dye in terms of its global production [1]. It results from the current fashion and necessity of using high amounts of dye when dyeing fabric to black. The final product is cheap because the synthesis of RB5 dye is easy and based on inexpensive semi-products. Its synthesis consists in the reaction of dosing in p-ester and double conjugation into 1-amino-8-hydroxy-3,6-disulfonic acid.

However, the industries who use this daily face problems with the treatment processes of wastewater that contain compounds of this type. The processes of dyeing cause that up to 15% of non-utilized colour compounds penetrate into the wastewater [2]. The dyes that have not been removed during technological processes migrate into the environment and are noticeable in natural waters, even at a concentration of 0.005 mg/dm³ [3].

Apart from the aesthetic aspect (the presence of intensive colour or colour suspensions), dyes also exert a toxic effect on the natural environment and on man [2, 4]. Dyes that enter the digestive system might cause liver, kidney and thyroid damage [5]. Some dyes have a carcinogenic effect [6]. Highly toxic are also the products of dye decomposition such as f.ex. aromatic amines, which are strongly methemoglobinoformative [7]. In the environment dyes disturb the penetration of light into water aquifers, thus impairing the biological processes at deeper water strata [8].

The biological methods of wastewater treatment most promoted often cannot be applied in practice. Frequently dyes exert toxic effects upon microorganisms responsible for the treatment process. Apart from the biotreatment of dye-containing wastewater, attempts are undertaken to treat it with physicochemical methods, including: chemical coagulation and flocculation, adsorption, ionic exchange, membrane processes, ozonation, and electrocoagulation [9, 10].

Electrocoagulation is a highly effective but also energy-consuming method [11]. Its advantages include no need for using chemicals during and after the treatment process, the significantly smaller construction space required and lower investment costs [12]. One drawback of this method is, however, the generation of vast amounts of sludge [11].

The mechanism of iron dosing into a solution is as follows [13, 14]:

Anode: $\quad F_{em} \rightarrow Fe^{2+} + 2e \quad$ (1)
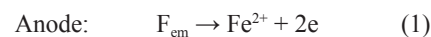
At pH above 6, iron 2+ ions present in the solution easily undergo oxidation with oxygen from the air according to the following reaction [15]:
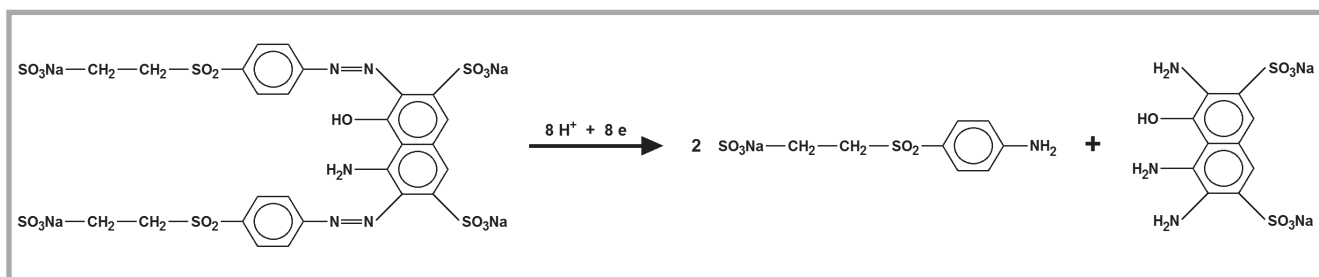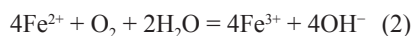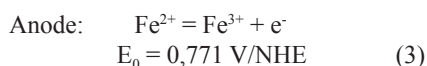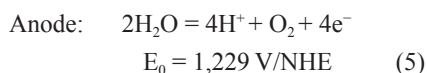
Figure 1. *Damage of nitrogen groups during hydrogen reduction on cathode.*

$$4Fe^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4OH^- \quad (2)$$

Consideration may also be given to the reaction of anode oxidation of Fe^{2+} [15]:

Anode: $\quad Fe^{2+} = Fe^{3+} + e^-$
$$E_0 = 0,771 \text{ V/NHE} \quad (3)$$

Processes of water electrolysis are also likely to occur on the anode and cathode [15]:

Cathode: $\quad 2H_2O + 2e^- = H_2 + 2OH^-$
$$E_0 = -0,828 \text{ V/NHE} \quad (4)$$

Anode: $\quad 2H_2O = 4H^+ + O_2 + 4e^-$
$$E_0 = 1,229 \text{ V/NHE} \quad (5)$$
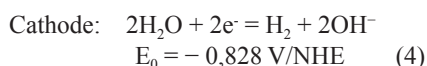
Hydrogen and hydroxyl ions also appear in the solution as a result of the electrolytic dissociation of water molecules.

$$H_2O = OH^- + H^+ \quad (6)$$

Hydrogen cations oriented towards the cathode will be subject to cathode processes that end in the production of hydrogen in either an atomic or molecular form [14, 16].

Cathode: $\quad 2H^+ + 2e^- = H_{2(g)} \quad$ pH > 7
$$\quad (7)$$

$$2H^+ + 2e^- = 2H_{(a)} \quad pH < 7$$
$$\quad (8)$$
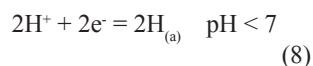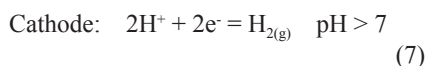
If atomic hydrogen is produced (8), it will form a protective layer (hydrogel polarization) that will inhibit the course of further electrochemical processes. If, for example, oxygen occurs in the solution, the atomic hydrogen may be bound

with it (oxygen depolarisation), and the process will continue. Depolarization may also be induced by other chemical compounds or microorganisms.

The mechanism of dye removal from a solution is more complex. Cations released on the anode may interact with dye molecules via electrostatic interaction, complexation and agglomeration (with hydroxides or other colloidal molecules formed in the solution) [17]. They may be directly adsorbed onto the surface of agglomerates that have been formed. Moreover they may undergo indirect and direct electrochemical reactions [4].

Apart from anode reactions, the cathode ones may also contribute to dye degradation [2]. Hydrogen released on the electrode may enhance the flocculation processes. In addition, damage to chromophore groups is likely to occur during the hydrogen reduction on the cathode through, for example, breaking nitrogen bonds or anthraquinone bonds [18, 19] (***Figure 1***).

An interesting alternative which does not require additional energy inputs seems to be the method of spontaneous oxidation of metals, e.g. zero-valent iron (ZVI). Also in this case, iron II ions migrate into the solution, and molecular or atomic hydrogen may be synthesised on the anode [14]. In the case of iron immersed in an aqueous solution, the rate of such

processes is higher or lower in the entire range of pH values. Iron is then subject to spontaneous electrochemical processes. The application of an external source of electric current to iron electrodes immersed in an aqueous solution (electrocoagulation) intensifies these processes even more. As demonstrated in earlier investigations, it is feasible to conduct processes of contaminant removal with no requirement for an external source of electric current [14, 16, 18].

Literature provides a number of comparative studies on electrocoagulation and conventional coagulation with the salts of metals [4, 11]. They address comparisons of the removal efficiencies of various contaminants (e.g. dyes, COD, turbidity-inducing compounds, phosphates, heavy metals etc.) and economical aspects of applying each of these methods. No comparative studies have, however, been conducted on electrocoagulation processes and the method based on the spontaneous oxidation processes of zero-valent iron. Considering the above, we compared two methods of RB5 dye removal, namely that of electrocoagulation and that based on the spontaneous electrochemical oxidation of zero-valent iron (ZVI).

■ Materials and methods

Double azo reactive dye (Reactive Black 5 – ***Tabele 1***) was provided by the dye production plant "Boruta", from Zgierz, Poland. Its stock solution was prepared as follows.

5 g of RB5 dye was weighed on an analytical scale and transferred quantitatively into a 5000 cm³ measuring flask. Working solutions of RB5 dye were prepared by diluting the stock solution with distilled water. The pH value (pH 3) was adjusted with a 0.1 M solution of HCl. The solutions were applied with the following concentrations: 25 mg RB5/dm³, 50 mg RB5/dm³ & 100 mg RB5/dm³.

Table 1. *Characteristics of Reactive Black 5 dye used in the study.*

Structural formula – RB5	Basic characteristics	
	Molar mass	991 g/mol
	λ_{max}	600 nm
	Other commercial names	Begazol Black B, Celmazol Black B, Diamira Black B, Intracron Black VS-B, Levafix Black E-B, Primazin Black BN, Remazol Black B, Sumifix Black B
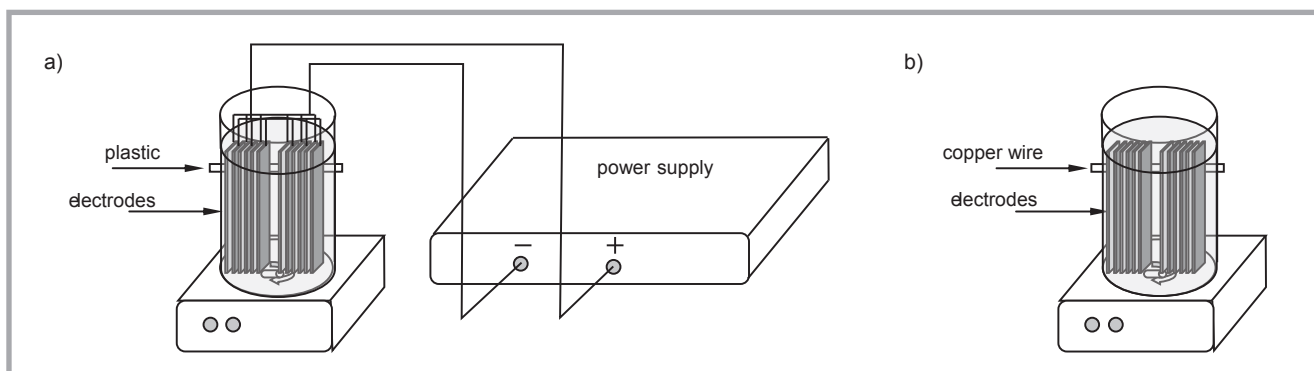
Figure 2. *Scheme of research station: a) reactor for electrocoagulation [EC], b) reactor for method based on zero-valent iron [ZVI].*

The single reactor used was composed of a cylindrical glass tank with a volume of 2500 cm³ and an MS 11HS magnetic stirrer by WIGO, with a stirring element in the form of a cylinder (ϕ 0.7 cm and length 5 cm) (**Figure 2**). The solution in the reactor was under continuous stirring at ca. 150 rpm.

The device was equipped with 5 anodes and 5 cathodes mounted alternately every 5 mm. The anodes were made of black steel, whereas the cathodes were of stainless steel (**Table 2**).

In the experiment with the electrocoagulation method [EC], an external source of electric current was applied to electrodes with an intensity of 0.1 A and voltage of 0.5 V (**Figure 2**). The electric current density was 0.14 mA/cm² and the total surface of electrodes immersed in wastewater was 1414 cm².

The feature that distinguished the reactor applied in the experiment with a method exploiting the oxidation processes of zero-valent iron from the reactor for EC was the lack of an external source of electric current. In this case, the electrodes were connected with a copper wire (1.5 mm in diameter).

The concentration of RB5 dye left in the solution was determined with the spectrophotometric method using a UV-VIS SP 2000 spectrophotometer at a wavelength of λmax = 600 nm. Samples were collected after: 0, 2, 5, 10, 20, 30, 60, 90, 120, 180, 240, 300, 360, 420, 480, 540, 600, 660, 720, 780, 840, 900, 960, 1080, 1200, 1320, 1440 & 1800 min.

Experimental data were described using three models – the Langmuir model, Langmuir 2 model and Freundlich model.

■ Langmuir model,

$$Qs = \frac{Q_{max} \cdot K_c \cdot C}{1 + K_c \cdot C}$$

■ Langmuir 2 model,

$$Qs = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C}$$

■ Freundlich model,

$$Qs = K \cdot C^n$$

Where: Q_s – mass of removed dye, mg/g Fe; Q_{max} – maximum sorption capacity in Langmuir equation, mg/g Fe; K_c – constants in Langmuir equation, dm³/mg; C – concentration of dye left in solution, mg/dm³; b_1 – maximum sorption capacity of sorbent (I type active sites), mg/g Fe; b_2 – maximum sorption capacity of sorbent (II type active sites), mg/g Fe; K_1; K_2 – constants in Langmuir 2 equation, dm³/mg; K – equilibrium constant in Freundlich model, dm³/mg; n – constant in Freundlich equation.

Constants in the Langmuir, Langmuir 2 and Freundlich equations were calculated with the use of Statistica 12.

The efficiency of dye removal (% U) was computed from the following **Equation (9)**:

$$\%U = \frac{c_o - c_f}{c_o} \cdot 100\% \qquad (9)$$

where: C_o and C_f – initial and final concentration of dye, mg RB5/dm³.

The kinetics of RB5 sorption in Fe is described with the use of:

■ pseudo-first order

$$\frac{dq}{dt} = k_1(q_e - q)$$

■ pseudo-second order equations

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

q – momentary quantity of sorbed RB5, mg/g Fe; q_e – equilibrium quantity of sorbed RB5, mg/g Fe; – sorption time, min; k_1 – constant in pseudo-first order equation, 1/min; k_2 – constant in pseudo-second order equation, mg/(g Fe · min).

All experiments were carried out at room temperature.

■ Results and discussion

The mechanism of dye removal is relatively complex and affected by various reactions occurring on the anode and cathode and in the solution [2]; however, both the EC method and ZVI method ensure a high efficiency of dye removal.

Effect of the method applied on dye removal efficiency

Three groups of solutions differing in the initial concentration of RB5 dye were analysed in the study. Over a 95% reduction in dye concentration was achieved in all cases. Electrocoagulation enabled over 98% efficiency of dye removal. It also ensured over a 95% reduction in dye concentration as early as after 180 min at the initial dye concentration of 25 mg RB5/dm³ and after 300 min at a dye concentration of 100 mg RB5/dm³ (**Figure 3**). The ZVI

Table 2. *Element composition of electrodes.*

Type of steel/ Type of electrode	Content, %								
	C	Mn	P	Al	N	S	Si	Cr	Ni
Black steel/Anode	0.130	0.52	0.011	0.043	0.006	0.005	–	–	–
Stainless steel/Cathode	0.024	1.64	0.027	–	0.049	0.002	0.39	10.1	8.1
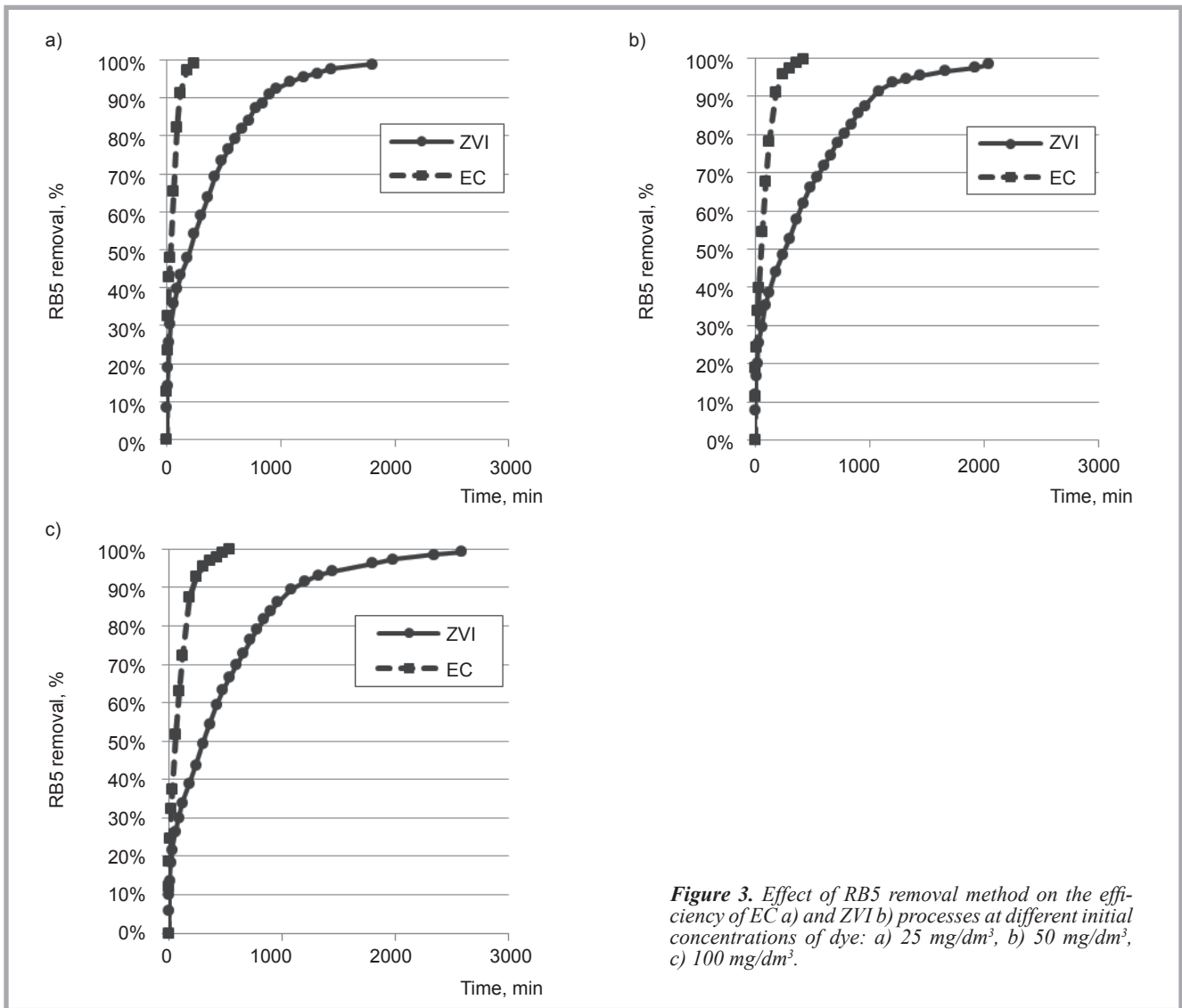
Figure 3. *Effect of RB5 removal method on the efficiency of EC a) and ZVI b) processes at different initial concentrations of dye: a) 25 mg/dm³, b) 50 mg/dm³, c) 100 mg/dm³.*

method requires a considerably longer contact time. Depending on the initial dye concentration, this method ensured over 95% dye reduction after 1200 min (25 mg RB5/dm³) and 1800 min (100 mg RB5/dm³) (**Figure 3**).

The contact time may, however, be shortened by increasing the contact area of dye solution with electrodes. Such attempts were undertaken during the removal of phosphorus compounds [20] or

carbon compounds, expressed as COD or BOD5, from the wastewater [21].

Effect of initial concentration of dye on its removal efficiency

The efficiency of colour removal is affected by the initial concentration of dye in the solution. An increase is observed in the removal efficiency along with decreasing values of the initial dye concentration. Significantly better effects of dye removal were achieved in the case of the ini-

tial dye concentration at 25 mg RB5/dm³ compared to 50 mg RB5/dm³ and 100 mg RB5/dm³. Such a correlation was observed for both methods applied, i.e. EC and ZVI (**Figure 4**).

Despite significant differences in the efficiency of dye removal, the sufficiently long process yielded similar final effects. Similar observations were made by Daneshvar et al. [8], who analysed the process of Orange II dye removal with the electrocoagulation method.

Effect of electrochemical processes on the efficiency of dye removal

In order to determine the effect of dye sorption on the post-electrolytic sludge, additional analyses were carried out with the sludge itself.

The process of electrolysis was conducted in an aqueous solution without the dye and resulted in iron ion migration into the solution.

Table 3. Constants determined from three models of dye sorption on post-electrolytic sludge.

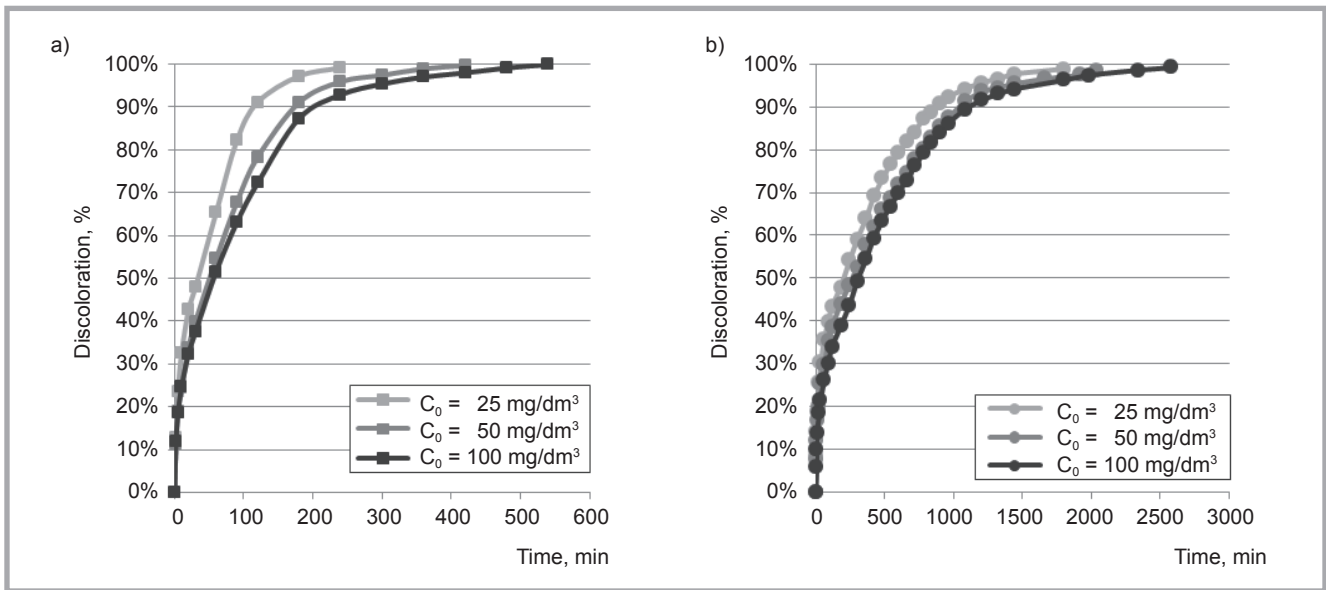| Determined constants					
Langmuir 2 model		**Langmuir model**		**Freundlich model**	
b_1, mg/g Fe	9672.71				
K_1, dm³/mg	0.00035	K_c, dm³/mg	0.00083	K, dm³/mg	358.92
b_2, mg/g Fe	1629.99				
K_2, dm³/mg	0.09357				
Q_{max} (b1 + b2), mg/g Fe	**11302.70**	Q_{max}, mg/g Fe	9888.96	n	0.3544
R^2	0.9983	R^2	0.9763	R^2	0.9944

Figure 4. *Efficiency of solution discoloration in time in experiments with a) EC and b) ZVI.*

In the aqueous solution and around the anode, the iron ions migrating to the solution will transform into various types of oxides, hydroxides etc. depending the on solution composition. Typical products of iron corrosion in water include [22-24]:

- goethite – α iron (III) hydroxide, (α-FeOOH),
- lepidocrite – γ iron (III) hydroxide, (γ-FeOOH),
- magnetite – iron (II) oxide, iron (III) oxide, (FeO · Fe_2O_3 lub Fe_3O_4),
- siderite – iron (II) carbonate, ($FeCO_3$),
- iron (III) hydroxide, ($Fe(OH)_3$),
- iron (II) hydroxide, ($Fe(OH)_2$).

The sludge thus obtained was mixed with an appropriate dose of dye.

Experimental results allowed to plot sorption isotherms with the use of three models (**Figure 5**, **Table 3**): the Langmuir model, Langmuir model and Freundlich model.

The best fit to experimental data was found for the Langmuir 2 model. The Langmuir 2 model implies the existence of at least two types of active sites, which are most likely iron ions of 2+ and 3+ degree of oxidation.

Further analyses involved a comparison of the effects obtained with the method of sorption on post-electrolytic sludge, and with the EC method (**Figure 6**).

The contribution of electrochemical processes in the removal of RB5 dye
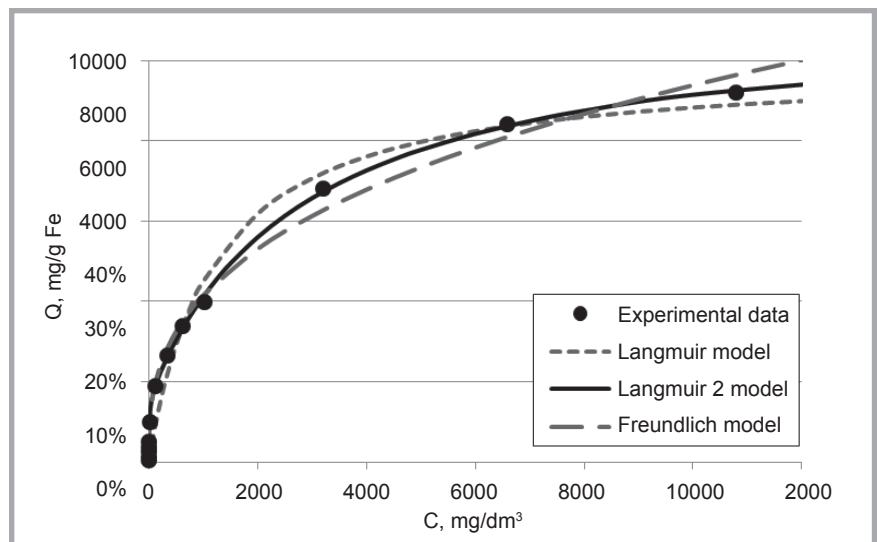

Figure 5. *Isotherms of RB5 dye sorption on post-electrolytic sludge.*

was observed to increase along with an increasing initial concentration of dye. At the lower dye concentration (25 mg RB5/dm³), the efficiency of its removal was similar to that obtained with the EC method only in the post-electrolytic sludge. Probably the sorption processes are significantly more rapid, and hence these processes dominate until the adsorption sludge is easily available. When the active centers deplete, electrochemical processes start to prevail.

Therefore it may be concluded that at lower dye concentrations, only sorption processes may facilitate removal efficiency, whereas at higher initial concentrations of dye, more efficient will be the

EC processes (sorption + electrochemical processes).

The sorption capacity of the post-electrolytic sludge calculated reached 11.30 g of RB5 per 1 g of solubilised iron.

The mass of iron dissolved into the solution was calculated based on the value of electric current and the electrolysis time using the following formula:

$$m_{Fe^{2+}} = \frac{It}{zF} \cdot M_{Fe} \qquad (10)$$

$m_{Fe^{2+}}$ – mass of iron ions released during electrolysis, g; I – electric current intensity, A; t – time of electrolysis, s; z – valency number of ions of iron (electrons
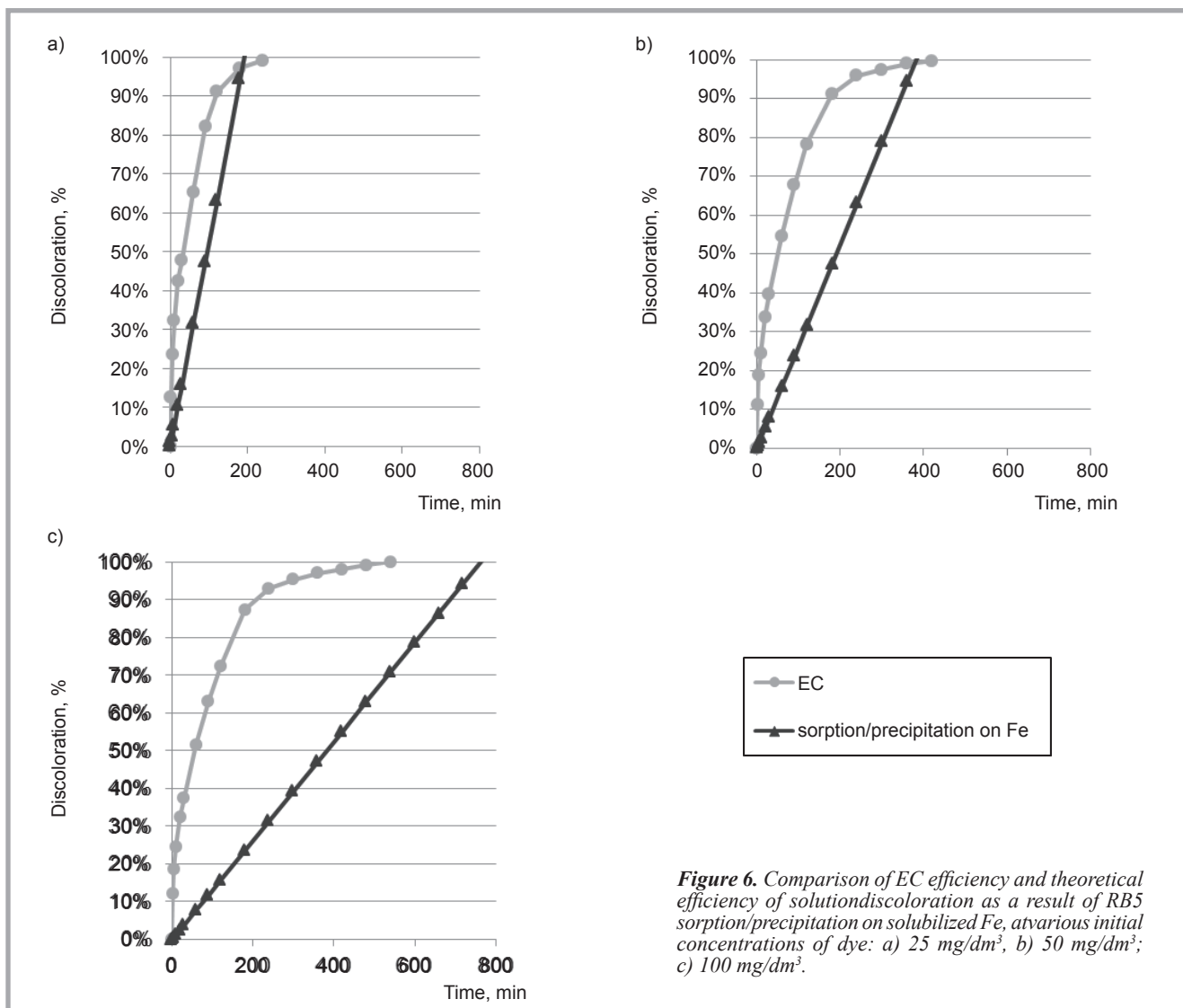
Figure 6. *Comparison of EC efficiency and theoretical efficiency of solutiondiscoloration as a result of RB5 sorption/precipitation on solubilized Fe, atvarious initial concentrations of dye: a) 25 mg/dm³, b) 50 mg/dm³; c) 100 mg/dm³.*

transferred per ion) = 2; F – Faraday's constant = 96,500 C; M_{Fe} – molar mass of iron, $g \cdot mol^{-1}$.

Comparison of the rate of EC and ZVI processes

Analyses of reaction kinetics play a significant role in planning the duration of dye removal from wastewater [25]. They allow to determine the solution retention time in the reactor. Knowledge of reaction kinetics is indispensable at the design stage as it enables to predict the rate of dye removal from the solution and, thus, the flow rate of the treated solution through the reactor as well as the size of the reactor required [26].

In the present study, we also determined the rate of RB5 dye removal reaction from solutions using both methods: ZVI and EC investigated.
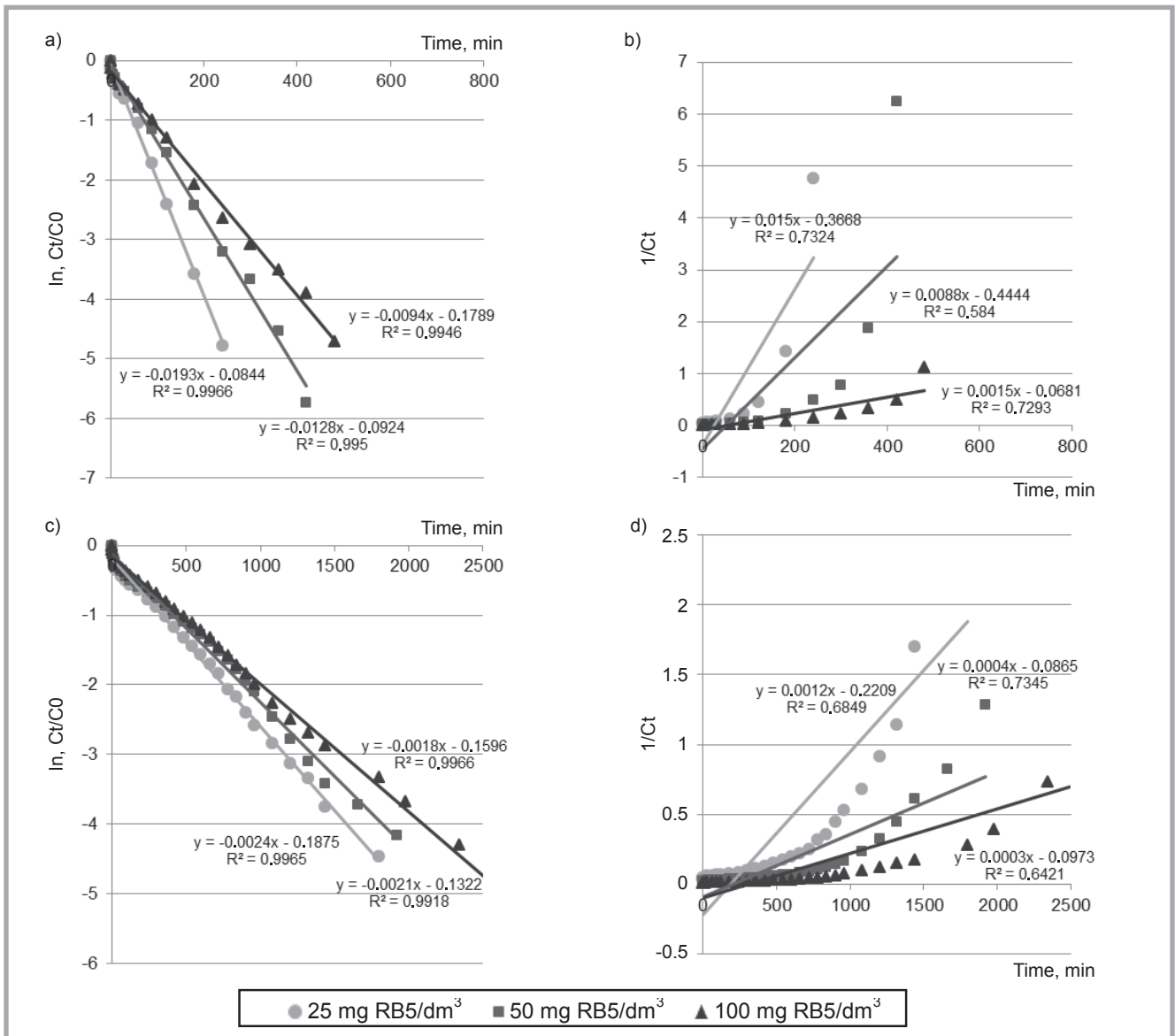
Firstly the order of reaction was established.

In both cases, these were pseudo – first order reactions (***Table 4***). The values of determination coefficient R^2 obtained allowed to conclude that the model of the pseudo – first order reaction showed better fit to experimental data. Afterwards reaction rate constants were determined and compared. As expected, the rate constant of dye removal from the solution was significantly higher during the electrocoagulation process (EC) (***Figure 7***).

In addition, the reaction rate constants decreased with an increasing initial concentration of dye in the solution. A similar observation was reported by Deb and Majumdar in their study on the removal of Novacron Red C4B dye with the use of aluminum electrodes. Perhaps it is linked with the availability of active centers on the adsorbent formed, namely on the post-electrolytic sludge.

Table 4. *Rate constants of RB5 dye removal from solution with EC and ZVI methods determined for the model of first and second order reactions.*

Method of decolorization	Initial dye concentration, mg RB5/dm³	Constants in pseudo-first order reaction model		Constants in pseudo-second order reaction model	
		k, 1/min	R²	k, mg /(g Fe · min)	R²
EC	25	0.0193	0.9966	15.0 x 10⁻⁴	0.7324
	50	0.0128	0.9950	8.8 x 10⁻⁴	0.5840
	100	0.0094	0.9946	1.5 x 10⁻⁴	0.7293
ZVI	25	0.0024	0.9965	1.2 x 10⁻⁴	0.6849
	50	0.0021	0.9918	0.4 x 10⁻⁴	0.7345
	100	0.0018	0.9966	0.3 x 10⁻⁴	0.6421

Figure 7. *Kinetics of RB5 removal from wastewater: a) EC – model of first order reaction (A), b) EC – model of second order reaction, c) ZVI – model of first order reaction, d) ZVI – model of second order reaction.*

The faster the process of metal digestion into the solution (e.g. faster in the case of EC compared to ZVI), the more sludge generated that may be used in sorption processes. The higher the initial concentration of dye, the greater the competition for active centers.

■ Conslusions

The analysis conducted demonstrated the feasibility of applying spontaneous corrosive processes of iron for colorant removal from the solution (RB5 dye). A similar removal efficiency to that with the use of electrocoagulation (EC) requires, however, a longer contact time or – as indicated by similar research [20] – a greater surface area of the electrodes applied. The efficiency of dye remov-

al is also determined by its initial concentration in the solution, i.e. the lower the initial dye concentration, the higher the efficiency of its removal. However, a long enough process ensures similar efficiency at all initial concentrations of dye with the use of both electrocoagulation methods and that based on spontaneous corrosive processes.

The study also demonstrated that the application of both the ZVI and EC methods is especially advisable at lower concentrations of dye in the solution. The higher the initial concentration of dye in the solution, the lesser the contribution of electrode processes in its removal from the solution. In turn, sorption processes are observed to prevail at higher initial concentrations of dye in the solution.

Results of determinations of the rate of dye removal reaction with the EC and ZVI methods enabled to conclude that these were I order reactions. As noticed earlier, the contribution of electrode processes in the mechanism of solution discoloration decreases at higher concentrations of RB5 in the solution. The increasing contribution of sorption processes proves this observation. The sorption processes are linked with the availability of active centers; and the greater the competition for these, the lower the reaction rate. The mechanism of dye removal from the solution requires, however, further investigations that will be addressed in future works of this research group.

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