



Adsorptive removal of acid, reactive and direct dyes from aqueous solutions and wastewater using mixed silica–alumina oxide

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ABSTRACT

Untreated or partially purified effluents from the textile, paper, plastic, leather, food and cosmetic industries containing dyes and pigments are a serious environmental problem. Therefore, in this paper, adsorptive removal of acid (C.I. Acid Orange 7, AO7), reactive (C.I. Reactive Black 5, RB5) and direct (C.I. Direct Blue 71, DB71) dyes from aqueous solutions and wastewater was investigated using mixed silica–alumina oxide consisting of 4% SiO₂ and 96% Al₂O₃ (SA96). Kinetic studies revealed that with the increasing initial dye concentration from 10 to 30 mg/L and contact time from 1 to 240 min, the sorption capacities (q_e) increased, and the equilibrium of adsorption for AO7 and RB5 was observed after 180 min and 240 min for DB71. Sorption of the dyes on SA96 takes place through the pseudo second-order mechanism rather than the pseudo first one or intraparticle diffusion. The experimental data fitted better the Langmuir isotherm model than the Freundlich one. The monolayer sorption capacities (Q_0) were found to be 41.4 mg/g, 47.1 mg/g and 49.2 mg/g for AO7, RB5 and DB71, respectively. The effect of the auxiliaries such as anionic surfactant (SDS) and sodium chloride on removal of DB71 was investigated in the 10 mg/L DB71 containing 0.1–1 g/L SDS or 5–20 g/L NaCl systems. It was observed that DB71 sorption was reduced with the increasing amount of SDS in the system while NaCl does not influence on the dye uptake by SA96. The adsorption of dyes causes increase of the solid surface charge density (σ_0) and shift of pH_{pzc} point toward higher pH values. This is a result of formation of a greater number of positive surface sites due to the interactions with the anionic adsorbate. The greatest effects were obtained for the system containing DB71. The addition of NaCl to the SA96–DB 71 system results in noticeable lowering of σ_0 in the pH range 4.4–8.3. In the presence of anionic surfactant, the considerable increase of σ_0 was obtained.

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1. Introduction

Synthetic mixed oxides have many important industrial applications. They are widely used as components of ceramics, fine optics, lasers, semiconductors, piezoelectrics, catalysts, nuclear fuels, pigments, etc. [1,2]. Due to their unique properties such as specific structure, high surface area and pore size, they are currently considered as effective, efficient, economic and eco-friendly adsorbents for removal of both organic and inorganic pollutants such as chlorophenols, complexones, polyelectrolytes and polymers, surfactants, dyes, metal ions and gases [3–8]. The adsorption of organic compounds like dyes on the mixed oxides provides a great challenge faced by scientists as these substances are dangerous for the environment because of toxicity and resistance to natural degradation. Taking into account the fact that more than 100 000 types of commercially available dyes exist and an annual world-wide production of 700 000–1000 000 tons has been reported, it is

difficult to imagine the amount of emitted colored effluents [9]. As estimated 280 000 tons of textile dyes is discharged as industrial wastewaters worldwide every year [9]. Thus, textile manufacturers paid attention to investment in wastewater treatment operation in order to reduce water consumption and residual level of recalcitrant organic pollutants in the fine effluents.

In this regard, the efficiency of mixed oxides toward removal of dye molecules has been studied in recent years. Khosravi and Eftekhari [10] evaluated the effectiveness of Na_{0.5}Li_{0.5}CoO₂ as the adsorbent for removal of methylene blue dye. Ninety-two percent of the dye was successfully removed in 10 min using 0.02 g Na_{0.5}Li_{0.5}CoO₂ at pH 11. A mixed oxide of cobalt and nickel of the approximate composition Co_{0.4}Ni_{0.4}O_{0.2} was applied for the methylene blue and procion red uptake with the sorption yield of 20% and 70%, respectively [11]. The azo dye Congo red sorption on the mixed iron and aluminum oxide as well as iron and nickel oxide was investigated by Mahapatra et al. [12] and Zeng et al. [13]. The remarkable sorption capacity of γ -Fe₂O₃-Al₂O₃ amounting 498 mg/g was determined [12]. Ni_{0.6}Fe_{2.4}O₄ was characterized by the fast sorption rate of Congo red (92% of the dye was removed within 9 min of contact time), but a lower value of maximum

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capacity (72.73 mg/g) was obtained [13]. Siliceous-based materials of natural occurrence and artificial origin were widely used for textile wastewaters treatment. Considering their chemical reactivity, porous structure, mechanical stability and high surface area, they can be attractive sorbents for dye-polluted waters [14,15]. Modified silicon dioxide possessed the highest affinity for C.I. Acid Blue 25 in comparison with the other organic pollutants such as p-nitrophenol, pentachlorophenol or 2,4-dichlorophenoxy acetic acid [16]. Silica-based sorbent (major constituents: 61.1% SiO₂, 22.6% Al₂O₃) was applied by Khan et al. [17] for sorption of methylene blue, malachite green and rhodamine B from aqueous solutions. The removal of dyes between 67.4% and 97.2% indicates that the sorbent is a moderately good one for the color elimination from the textile wastewaters [17]. The fly ash as a by-product generated during the coal combustion in thermal power plant, consisting of silicon dioxide (43.7%), aluminum oxide (15.7%), iron oxide (6.4%), calcium oxide (9.8%) and magnesium oxide (0.9%) was evaluated as efficient sorbent for methylene blue removal [18]. Titania-silica mixed oxide was applied for removal of C.I. Basic Violet 10 with the sorption capacity ranged from 10.5 to 32.1 mg/g depending on the molar ratio of TiO₂ to SiO₂ [19]. TiO₂-SiO₂ combined with manganese or cobalt ions was shown to be more effective in sorption of C.I. Disperse Red 19 than undoped titanium-silica oxide, despite the higher surface area of the latter [20].

As improper treatment and disposal of dye-contaminated effluents provoked serious environmental concerns all over the world, the adsorption behavior of three different textile dyes of anionic type (C.I. Acid Orange 7, C.I. Reactive Black 5, C.I. Direct Blue 71) onto the mixed alumina-silica oxide was investigated. Such parameters as initial dye concentration, phase contact time, solution pH and presence of surfactant influenced the dye adsorption. Mixed oxides are considered not effective adsorbents for dye removal because there is an opinion that they cannot absorb a wide range of dyes and perform poorly in the presence of other additives. Such view is erroneous since at least one successful treatment is known. The relatively good sorption results presented in this paper suggest that mixed silica-alumina oxides could be efficient sorbents for dye removal. Therefore, the authors are convinced that the experimental results contribute to the studies on the mechanism of dye sorption on mixed oxides, particularly including the effects of salt and surfactant addition which are frequently found in real wastewaters.

2. Experimental

2.1. Chemicals

The chemicals were purchased from Sigma-Aldrich (Germany) or POCh (Poland) and used without further purification. Doubly distilled water was used throughout.

The short characteristics of three textile dyes are as follows: C.I. Acid Orange 7 (sodium salt of 4-(2-hydroxynaphthylazo)benzenesulfonic acid), C.I. Reactive Black 5 (tetrasodium salt of 4-amino-5-hydroxy-3,6-bis((4-((2-(sulfoxy) ethyl)sulfonyl)phenyl)azo)-2,7 naphthalenedisulfonic acid) and C.I. Direct Blue 71 (tetrasodium 3-[(E)-{4-[(E)-{4-[2-(6-amino-1-oxo-3-sulfonatophthalen-2(1H)-ylidene)hydrazino]-6-sulfonatophthalen-1-yl]diazetyl]naphthalen-1-yl]diazetyl]naphthalene-1,5-disulfonate) are presented in Fig. 1.

The samples of mixed alumina-silica oxide of the chemical composition: Al₂O₃ (96%) and SiO₂ (4%) were used in the study (pilot plant in the Chuiko Institute of Surface Chemistry, Kalush, Ukraine). The applied oxide was prepared using the CVD method (Chemical Vapour Deposition) [21]. The alumina-silica oxide will be abbreviated to SA96. The adsorbent was characterized by the BET surface area of 75 m²/g and the mean pore diameter of 7.4 nm. Both parameters were determined by the low-temperature nitrogen adsorption-desorption isotherm method (Micromeritics ASAP 2405 analyzer, USA).

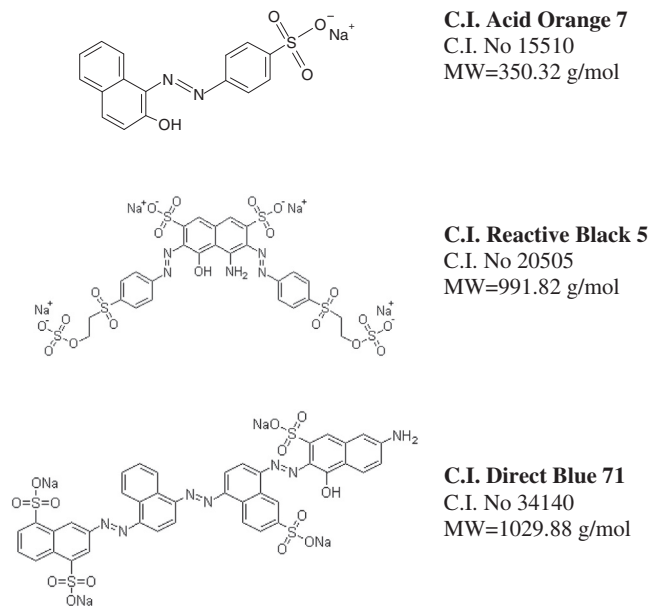


Fig. 1. Structural formula of the dyes used.

2.2. Measurements of kinetic and equilibrium adsorption parameters

In order to determine kinetic parameters, the samples (20 mL of the solution of the initial dye concentrations 10, 20 and 30 mg/L and 0.02 g of SA96) were mixed at different time intervals (0–240 min). Next they were filtered off under vacuum and taken for UV-vis spectrophotometer Specord M-42 (Carl Zeiss, Germany) analysis at the maximum absorbance wavelengths (484 nm, 587 nm and 598 nm for C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71, respectively).

The effect of phase contact time on the decolorization of the raw textile wastewater after the ozonation step obtained from the textile company was investigated using the batch method, too. The composition of the industrial dye bath was as follows: C.I. Reactive Black 5 (6.25 g/L), Na₂CO₃, NaOH, NaCl and Perigen LDR (liquid dispersing and sequestering agent); wastewater after the ozonation step of pH 6.64. In this experiment, the dosage of 0.02 g of mixed oxide was shaken with 20 mL of the wastewater for 3 to 69 h. During this experiment, small samples were withdrawn after various phase contact times in order to estimate the color removal by the analysis of absorbance values at the maximum absorbance wavelength. The spectra were recorded after 10 times dilution.

Equilibrium sorption experiments were carried out in the following conditions: 0.02 g of SA96 adsorbent was mixed with a 20 mL of the dye solution at 25 °C (each reaction was performed three times, and displayed a relative standard deviation lower than 4.34%). Stock solutions of dyes were prepared from analytical reagent products and then were diluted to give a series of solutions of different concentrations. The time required to work in equilibrium was determined by preliminary kinetic measurements and equaled 240 min.

The effect of such auxiliaries as sodium chloride and sodium dodecyl sulfate (SDS) on the amount of dye retained by SA96 at equilibrium was studied shaking 0.02 g of SA96 with 20 mL of the solution containing 10 mg/L dye and 5–20 g/L NaCl or 0.1–1 g SDS for 240 min.

The amounts of the dyes adsorbed after different time intervals (q_t) and at equilibrium (q_e) on SA96 were calculated from the difference between the dye concentration in the solution before and after the adsorption process and were expressed in mg/g.

2.3. Measurements of surface charge density

The potentiometric titration method was used to determine the surface charge of the mixed oxide in water and dye solutions (also in the presence of NaCl and SDS). This method is based on the comparison of the titration curve of water with that of suspension (water containing an adsorbent). Such comparison of both titration curves allows determination of the pH_{pzc} (pzc—point of zero charge)—it is located at the intersection of these two curves. The surface charge density (σ_0) is determined from the difference in the volume of base (ΔV) which must be added to bring the pH of suspension and water to the specified value:

$$\sigma_0 = \frac{\Delta V c_b F}{mS} \quad (1)$$

where c_b (mol/L)—base concentration, F (C/mol)—Faraday constant, m (g)—solid mass in the suspension, S (m^2/g)—specific surface area of the solid.

The set for these measurements was composed of the following parts: Teflon vessel, burette Dosimat 665 (Methrom, USA), thermostat RE204 (Lauda, France), pH-meter 71 (Beckman, UK) connected with the computer and printer. The solid surface charge density was calculated with the special program *titr_v3* (author W. Janusz).

0.15 g of the SA96 oxide was added into the thermostated vessel ($25^\circ\text{C} \pm 0.1$) up to 50 mL of the examined dye solution or only to the water. The suspensions prepared in such a way were titrated with the NaOH solution (0.1 mol/L) in the pH range 3–10. The solid surface charge density was calculated numerically using the titration curve of water (obtained at the beginning of the potentiometric titration experiments).

The potentiometric titrations were carried out for the solutions of three dyes: C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 at their concentrations 10, 20 and 30 mg/L. Due to the fact that C.I. Direct Blue 71 shows the largest adsorption on the solid surface, the influence of salt (NaCl) and surfactant addition was examined for this dye at its concentration 10 mg/L. The following concentrations of salt and surfactant were applied: 5, 10, 15, 20 g/L (NaCl) and 0.1, 0.25, 0.5, 0.75, 1.0 g/L (SDS).

3. Results and discussion

3.1. Kinetic studies

One of the most important characters of efficient adsorbent is high rate of adsorption. Fig. 2 presents the effect of shaking time (0–240 min) on the adsorption of acid, reactive and direct dyes from the solutions of different initial dye concentrations (10–30 mg/L). It can be seen that the amount of dyes adsorbed increase with the increasing contact time and the initial dye concentration. The studies revealed that majority of C.I. Acid Orange 7 and C.I. Reactive Black 5 were removed within the first 60 min of contact time whereas for C.I. Direct Blue 71 the time was three times longer. The fast adsorption of the dyes during the initial stages of sorption is due to the high concentration gradient between the adsorbate in solution and that on the adsorbent as there is a large number of available vacant sites. After 180 min, the plateau was observed for C.I. Acid Orange 7 and C.I. Reactive Black 5, which is related to a slow rate of adsorption, which could be due to agglomeration of the dyes on the active sites of the mixed oxide. The static equilibrium of adsorption for C.I. Direct Blue 71 occurred after 240 min of phase contact time. According to Sarma et al. [22], the equilibrium time depends on the molecular weight and the structural complexity of dye molecules. The great affinity of C.I. Reactive Black 5 and C.I. Direct Blue 71 for SA96 was expressed in high values of q_t . For C.I. Reactive Black 5, the amounts of dye adsorbed at equilibrium were 6.8 mg/g, 7.2 mg/g and 9.7 mg/g for the solutions of the initial concentrations 10 mg/L, 20 mg/L and 30 mg/L, respectively. The amounts of the direct dye retained by SA96 increase from 1.1 to 6.4 mg/g, from 2.1 to

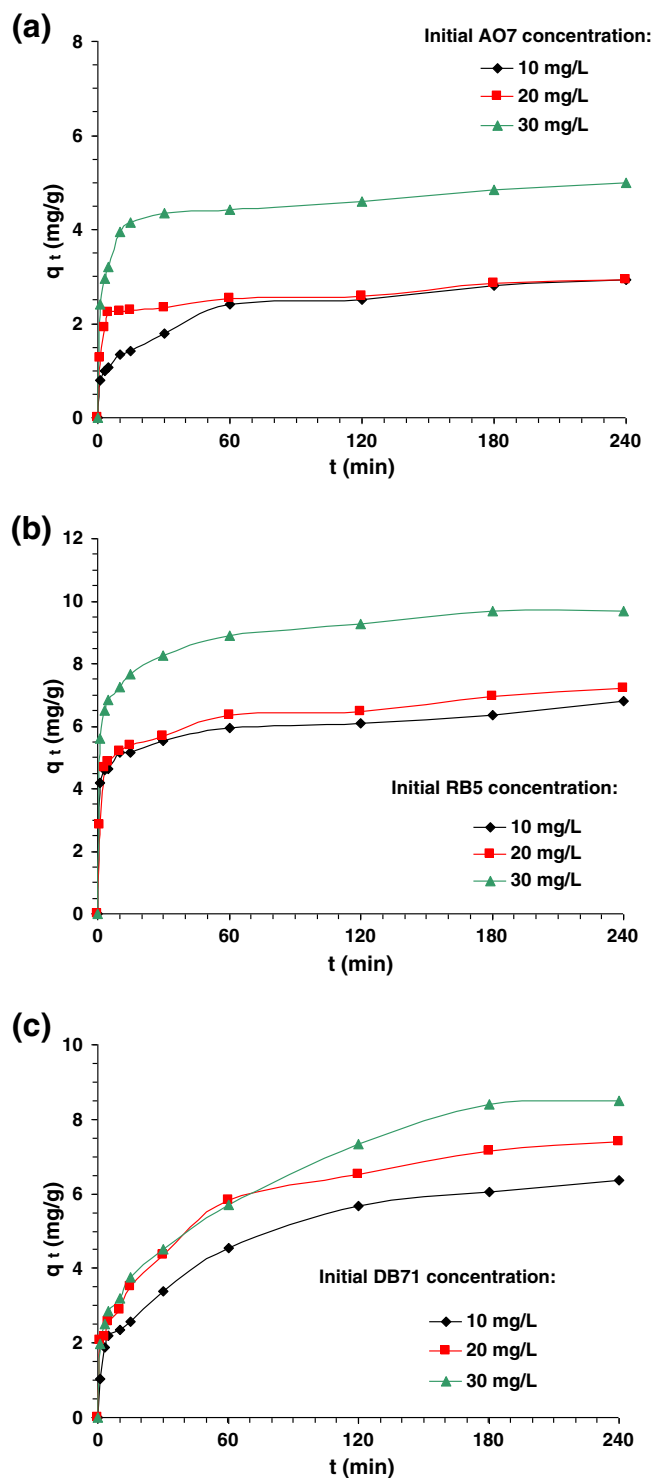


Fig. 2. Kinetic data for the adsorption of (a) C.I. Acid Orange 7, (b) C.I. Reactive Black 5 and (c) C.I. Direct Blue 71 by SA96 at different initial concentrations.

7.4 mg/g and from 2.0 to 8.5 mg/g with the increasing initial concentrations from 10 to 30 mg/L.

In order to interpret the mechanism of dye retention, the empirically obtained kinetic sorption data were fitted to the Lagergren pseudo first-order (PFO), Ho and McKay pseudo second-order (PSO) and Weber–Morris intraparticle diffusion (IPD) models using Eqs. (2)–(5) as follows [23–26]:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

$$h = k_2 q_e^2 \quad (4)$$

$$q_t = k_{id} t^{0.5} \quad (5)$$

where k_1 (1/min), k_2 (g/mg min) and k_{id} (mg/g min^{0.5}) are the adsorption rate constants of pseudo first-order, pseudo second-order and intraparticle diffusion models, respectively; h (mg/g min) is the initial sorption rate; q_e (mg/g) is the dye uptake at equilibrium; and q_t (mg/g) is dye uptake at time t .

Using Eq. (2), $\log(q_e - q_t)$ was plotted against t in order to calculate the pseudo first-order rate constant k_1 . From the slope and intercept of the plot t/q_t vs t , the pseudo second-order rate constants k_2 and q_e were computed, respectively. The intraparticle diffusion rate constant was obtained from the slope of the plot q_t vs $t^{0.5}$.

The calculated kinetic parameters for the adsorption of the acid, reactive and direct dyes on SA96 at three different initial concentrations are listed in Table 1. The pseudo first-order rate coefficients of 0.020 to 0.081 1/min indicated an appreciable fast reaction. However, it was found that the experimentally obtained q_e values did not match those determined from the Lagergren plots. There existed a very large deviation reflected in the values of determination coefficients ranging from 0.633 to 0.979. Therefore, it is more likely that the adsorption of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 on SA96 might take place through the second-order mechanism.

The pseudo second-order rate constants ranged from 0.021 to 0.296 depending on the dye type and its initial concentration. The experimental and theoretical q_e values matched each other with a small deviation from linearity. The determination coefficients were found to be from 0.964 to 0.999 for C.I. Acid Orange 7, from 0.997 to 0.998 for C.I. Reactive Black 5 and from 0.961 to 0.998 for C.I. Direct Blue 71 compared to the initial dye concentration from 10 to 30 mg/L (Table 1). Good compliance of the obtained data with the pseudo second-order equation indicates that the chemical reaction is significant in the rate-controlling step. However, according to Allen et al. [27], physical adsorption and chemisorption may be indistinguishable in certain situations despite high R^2 values and in some cases a degree of both types of bonding can be present. The applicability of the pseudo second-order model in describing sorption kinetic data of methyl orange on the organometallic functionalized SiO₂-Al₂O₃ and on the ordered mesoporous alumina was confirmed by Arshadi et al. [28] and Yahyaei et al. [29], respectively. The studies performed by Banerjee et al. [18] indicated that the pseudo second-order model was more consistent with the experimental data of sorption kinetic of methylene blue on activated fly ash mainly consisting of silicon and aluminum oxides. The same observations were described by Anabia and Salehi [30] for C.I. Acid Blue 113, C.I. Acid Red 114, C.I. Acid Green 28, C.I. Acid Yellow 127 and C.I. Acid Orange 67 sorption on the functionalized silica.

In order to find out if the adsorption of the acid, reactive and direct dyes on SA96 takes place inside the pores by a diffusion mechanism (Eq. (5)), the plots of q_t vs $t^{0.5}$ were drawn. The intraparticle diffusion rate coefficients were in the range from 0.233 to 0.776 mg/g min^{0.5}. Despite having good linearity (range of R^2 values from 0.926 to 0.996), these plots had nonzero intercepts and therefore the intraparticle diffusion could not play a major role in retention of the dyes by SA96.

Table 1

Kinetic parameters for the adsorption of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 on mixed silica–alumina oxide.

| Dye | C ₀ | q _{e,exp} | Pseudo first-order constants | Pseudo second-order constants | Intraparticle diffusion constants |
|-----------------------|----------------|--------------------|------------------------------|-------------------------------|-----------------------------------|
| C.I. Acid Orange 7 | 10 | 2.9 | k ₁ 0.023 | k ₂ 0.055 | k _{id} 0.233 |
| | | | q _e 2.2 | q _e 2.5 | R ² 0.996 |
| | | | R ² 0.947 | h 0.35 | |
| | 20 | 2.9 | k ₁ 0.053 | R ² 0.964 | |
| | | | q _e 1.4 | k ₂ 0.296 | k _{id} 0.776 |
| | | | R ² 0.633 | q _e 2.6 | R ² 0.993 |
| | 30 | 5.0 | | h 2.0 | |
| | | | k ₁ 0.081 | R ² 0.999 | |
| | | | q _e 2.7 | k ₂ 0.152 | k _{id} 0.696 |
| C.I. Reactive Black 5 | 10 | 6.8 | R ² 0.975 | q _e 4.5 | R ² 0.992 |
| | | | | h 3.08 | |
| | | | k ₁ 0.030 | R ² 0.999 | |
| | 20 | 7.2 | q _e 2.7 | k ₂ 0.113 | k _{id} 0.233 |
| | | | R ² 0.881 | q _e 6.0 | R ² 0.996 |
| | | | | h 4.1 | |
| | 30 | 9.7 | k ₁ 0.044 | R ² 0.998 | |
| | | | q _e 3.8 | k ₂ 0.077 | k _{id} 0.774 |
| | | | R ² 0.690 | q _e 6.4 | R ² 0.988 |
| C.I. Direct Blue 71 | 10 | 6.3 | h 3.2 | R ² 0.997 | |
| | | | k ₁ 0.031 | k ₂ 0.063 | k _{id} 0.696 |
| | | | q _e 5.1 | q _e 9.0 | R ² 0.981 |
| | 20 | 7.4 | R ² 0.912 | h 5.1 | |
| | | | k ₁ 0.020 | R ² 0.998 | |
| | | | q _e 5.0 | k ₂ 0.026 | k _{id} 0.462 |
| | 30 | 8.5 | R ² 0.758 | q _e 4.9 | R ² 0.926 |
| | | | | h 0.624 | |
| | | | k ₁ 0.021 | R ² 0.961 | |
| | 10 | | q _e 5.8 | k ₂ 0.021 | k _{id} 0.537 |
| | | | R ² 0.979 | q _e 7.2 | R ² 0.979 |
| | | | | h 0.807 | |
| | 20 | | k ₁ 0.021 | R ² 0.983 | |
| | | | q _e 6.4 | k ₂ 0.027 | k _{id} 0.555 |
| | | | R ² 0.963 | q _e 8.1 | R ² 0.990 |
| | 30 | | | h 1.0 | |
| | | | | R ² 0.998 | |
| | | | | | |

C₀ (mg/L), q_{e,exp} (mg/g), k₁ (1/min), k₂ (g/mg min), h (mg/g min), k_{id} (mg/g min^{0.5})

Transport from the bulk phase to the adsorbent surface and diffusion to the interior through pores are the two processes, which can occur simultaneously. If the steps are independent, the plots usually have two or three intersection lines, depending on the mechanism [22]. The first line represents the surface adsorption and the second one the intraparticle diffusion. No such sectionalization was observed in the plots of this paper. The Weber–Morris intraparticle diffusion model also failed in describing the rate-controlling step of sorption kinetics of methylene blue on the mixed oxide [18].

In order to emphasize the influence of phase contact time on the textile effluents purification by SA96, the raw wastewater sample was equilibrated with the mixed oxide for the period of 1 h to 96 h. The wastewater UV–vis spectra before and after sorption were recorded and are shown in Fig. 3. Decolorization of wastewater on the level of 30% was obtained after 96 h. 5.5%, 13.8%, 18.75 and 24% color reduction was observed after 6 h, 12 h, 24 h and 48 h of phase contact time, respectively. It was also observed that further increase of phase contact time did not enhance the purification yield using SA96. The yield of raw wastewater purification is very important information taking into consideration the applicability of such sorbent in the sewage-treatment plant with the adsorptive precipitation step.

3.2. Equilibrium studies and adsorption mechanism

The discussion of the equilibrium adsorption state is very important as it allows to understand the adsorption mechanism. Thus, the experimental equilibrium data of the retention of the acid, reactive and direct dye on SA96 were fitted using the Freundlich and Langmuir isotherm models which are typically used for aqueous phase adsorption and are expressed by Eqs. (6) and (7):

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (7)$$

where q_e (mg/g) is the amount of dye uptake by the sorbent at equilibrium, C_e (mg/L) is the dye concentration at equilibrium, k_F (mg/g) and $1/n$ are the Freundlich constants, Q_0 (mg/g) and b (L/mg) are the Langmuir constants.

The Langmuir isotherm model assumes the monolayer coverage of sorbed molecules on a solid surface with no or very weak intermolecular forces decreasing with the distance from the adsorption surface,

whereas the Freundlich model relates to the multilayer adsorption with interactions between adsorbates on the heterogeneous surface.

It was observed that the obtained experimental data best match the Langmuir isotherm rather than the Freundlich one (Fig. 4, Table 2). It was confirmed by the values of the determination coefficients R^2 being in the range 0.992–0.999. The monolayer sorption capacities Q_0 were found to be 41.4 mg/g, 47.1 mg/g and 49.2 mg/g for C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71, respectively. The high affinity of C.I. Direct Blue 71 for SA96 is confirmed by in the b value equal to 0.549, which reflects the strongest interactions and stable adsorption product amidst the investigated dyes. On the basis of the monolayer sorption capacities Q_0 and the Langmuir constants b related to the free energy of adsorption, the affinity series of the dyes for the fumed silica–alumina oxide SA96 can be presented:

C. I. Direct Blue 71 > C. I. Reactive Black 5 > C. I. Acid Orange 7

The Langmuir isotherm model fits better the experimental values of sorption compared to the other models in the following systems: methylene blue–poplar leaf, methyl orange–activated clay, C.I. Reactive Black 5–green alga *Chlorella vulgaris* [14]. Contrary to these observations, the Freundlich isotherm model was found to be more suitable for explanation of acidic dye adsorption on the modified silica [30].

Surface properties of mixed silica–alumina oxides depending on the concentration of silica and alumina phases were broadly investigated using different methods and described by Zarko et al. [31], Gun'ko et al. [32,33] and Hensen et al. [34]. On the surface of the mixed oxide, regions rich in silica or alumina can occur with the $-\text{OH}$ and $-\text{OH}_2^+$ groups as well as oxygen bridges depending on solution pH. The structure of the adsorbent surface having various functional groups must be taken into account to elucidate the adsorption mechanisms. The dye structure is also not without importance as they contain different chromophores and auxochromes, e.g., sulfonic ones, which are dissociated in the aqueous medium forming $R(\text{SO}_3)_n^{n-}$ and $n\text{Na}^+$. In this context, it is necessary to mention that the used dyes belong to anionic ones containing not only sulfonic groups, but also functional amine, hydroxyl, azo and vinylsulfonyl or 2-sulfoxyethylsulfonyl functional ones. Considering the structure of the adsorbates and the adsorbent, it was assumed that the retention mechanism of dyes by mixed silica–alumina oxide involved electrostatic interactions between the negatively charged sulfonic group of the dyes and the positively charged protonated hydroxyl group of mixed oxide, hydrogen bonding between S, O, N atoms present in the functional groups of the dyes as well as aromatic rings and $-\text{OH}$ (or $-\text{OH}_2^+$) groups of mixed oxide and van der Waals forces. Fig. 5 presents a possible mechanism of C.I. Direct Blue 71 interactions with mixed silica–alumina oxide. The above adsorption mechanism was also proposed for methylene blue sorption on the mixed oxide of SiO_2 and Al_2O_3 as the main components [18].

3.3. Effect of auxiliaries presence

It is well known that auxiliaries such as surfactants and inorganic electrolytes are added to the dye bath. Surfactants affect dyeing parameters like stability of dye bath, extent of dyeing, dyeing rate and uptake by the fiber, etc. [35–37]. Inorganic electrolytes decrease negative electrokinetic potential ζ of the fiber and facilitate the access of the dye anions into the fiber surface. Therefore, huge amounts of inorganic salts are discharged to the textile effluents. For this reason, the effect of the anionic surfactant (SDS) and sodium chloride, on the C.I. Direct Blue 71 of the highest affinity for mixed oxide, was investigated. Fig. 6 compares the uptake of C.I. Direct Blue 71 by SA96 in the absence or presence of these substances in the systems containing 10 mg/L of dye and from 5 to 20 g/L of NaCl or from 0.1 to 1 g/L of SDS.

It was observed that sorption of C.I. Direct Blue 71 was reduced with the increasing amount of SDS in the system. The amount of the dye

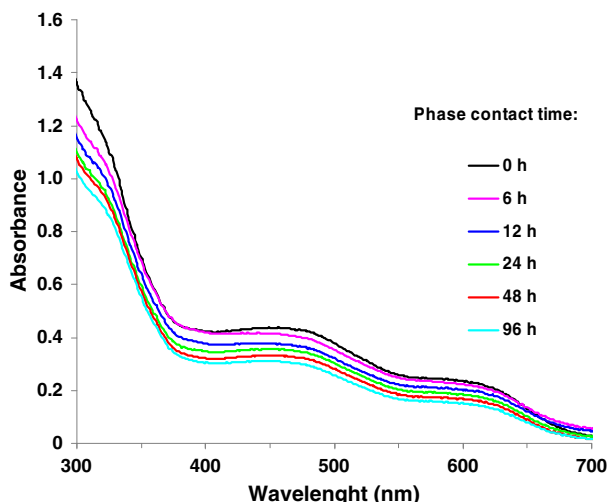


Fig. 3. Influence of contact time on raw wastewater decolorization using SA96.

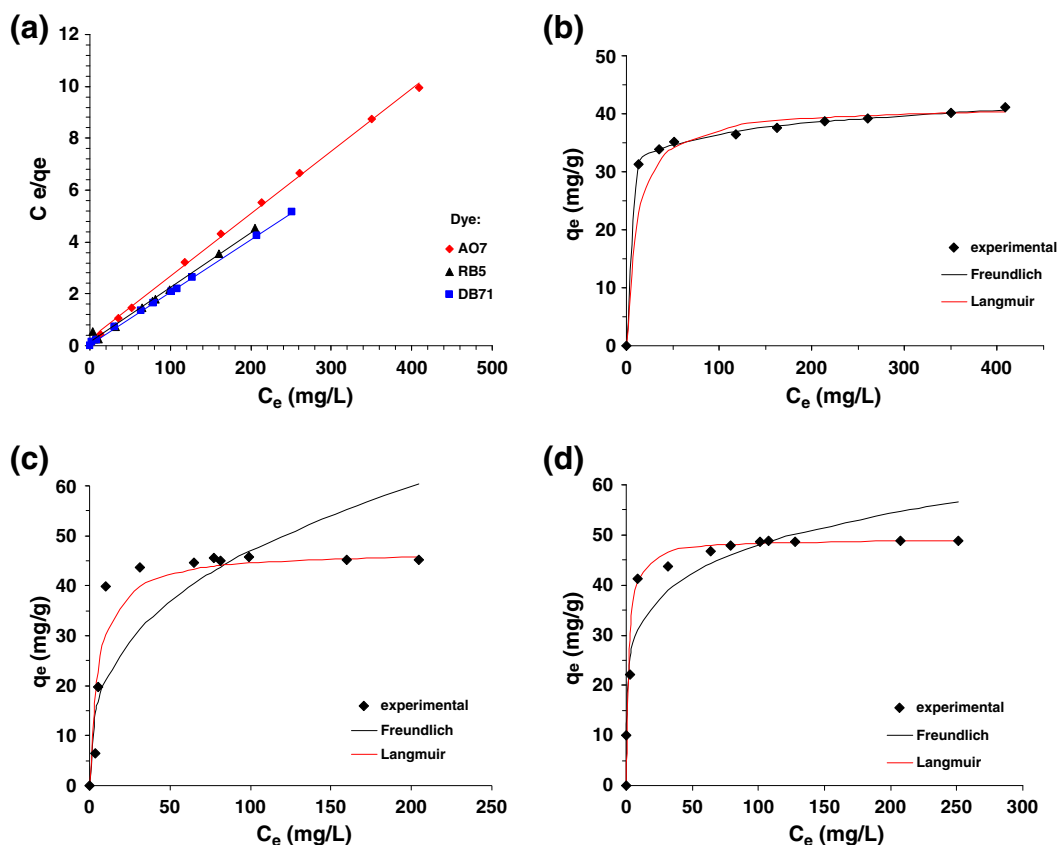


Fig. 4. Langmuir adsorption isotherms (a) and the fitting of the isotherm models to the experimental sorption data of (b) C.I. Acid Orange 7, (c) C.I. Reactive Black 5 and (d) C.I. Direct Blue 71.

retained by SA96 decreases from 6.4 mg/g to 0.61 mg/g with the increasing amount of SDS from 0.1 g/L to 1 g/L, respectively. The anionic surfactant SDS and the dye anions bearing the same charge compete for sorption sites on the surface of SA96 therefore reduction of the dye uptake is observed. Increasing surfactant concentration, the solubilization of the dye into the micelles of surfactant also occurred leading to decrease of free dye anions which are accessible to the surface of the mixed oxide.

The presence of sodium chloride does not affect the adsorption of C.I. Direct Blue 71 by SA96 in the investigated concentration range.

3.4. Surface charge density studies

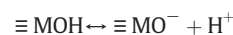
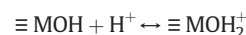
Dye adsorption behavior considerably depends on the type and concentration of surface groups of the adsorbent. The solid surface charge is a total charge of all types of these groups whose concentration varies with the increasing solution pH.

Table 2

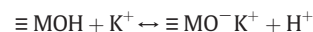
Isotherm parameters determined for the acid, reactive and direct dye sorption on the mixed silica–alumina oxide SA96 at equilibrium.

| Isotherms | C.I. Acid Orange 7 | C.I. Reactive Black 5 | C.I. Direct Blue 71 |
|-------------------------|--------------------|-----------------------|---------------------|
| <i>Langmuir model</i> | | | |
| Q_0 (mg/g) | 41.4 | 47.1 | 49.2 |
| b (L/g) | 0.091 | 0.176 | 0.549 |
| R^2 | 0.999 | 0.992 | 0.999 |
| <i>Freundlich model</i> | | | |
| k_F (mg/g) | 25.7 | 9.3 | 21.1 |
| $1/n$ | 0.076 | 0.351 | 0.178 |
| R^2 | 0.991 | 0.630 | 0.937 |

Water molecules present in the solution cause the hydroxylation of a metal oxide surface M (where M —Si or Al) [38,39]. Surface hydroxyl groups are amphoteric and therefore can connect or disconnect proton according to the reactions:



The reactions involving electrolyte (salt) ions can also take place. As a result, the connections of surface complexes or ion pairs are formed. Surface complexes are formed according to the equations:



On the other hand, ion pair connections are formed in the following way:



The presence of other ionic substances, such as dyes or surfactants at the metal oxide–solution interface can significantly change the structure and properties of the electrical double layer, affecting the surface charge. The binding process of these compounds with the solid surface takes place analogously to that of the electrolyte ions. In the case of anionic dyes and surfactants, this can be represented as

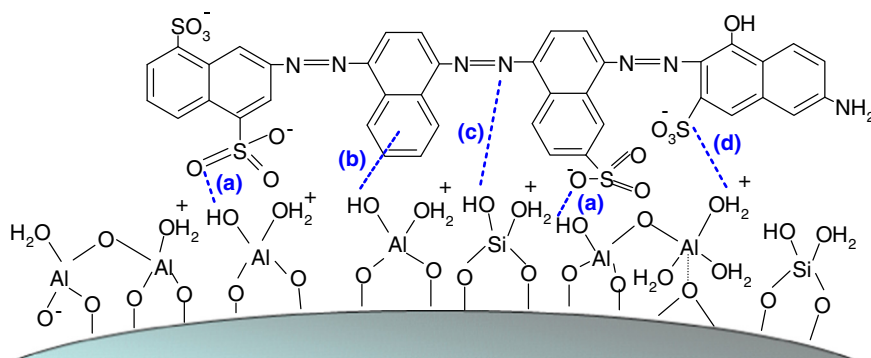
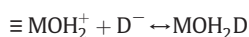


Fig. 5. Schematic representation of interactions of mixed oxide SA96 with C.I. Direct Blue 71 in the acidic medium: (a) hydrogen bonding between the hydroxyl group of SA96 and oxygen atoms of in dye molecule, (b) hydrogen bond between the hydroxyl group of SA96 and the aromatic ring in the dye, (c) hydrogen bond between the hydroxyl group of SA96 and the azo group of the dye, (d) ion pair between the protonated hydroxyl group of SA96 and dissociated sulfonic group of the dye.

follows (where D is the dye molecule and S is the surfactant molecule):



Therefore, the surface charge of solid is the sum of charges of all components of the system adsorbed on the metal oxide surface. For

example, for the system containing dye in salt or surfactant solution, σ_0 can be expressed as

$$\sigma_0 = \sigma_{\text{solid_ionized_groups}} + \sigma_{\text{salt_counterions}} + \sigma_{\text{dye_ionized_groups}} + \sigma_{\text{dye_counterions}}$$

$$\sigma_0 = \sigma_{\text{solid_ionized_groups}} + \sigma_{\text{surfactant_ionized_groups}} + \sigma_{\text{surfactant_counterions}} + \sigma_{\text{dye_ionized_groups}} + \sigma_{\text{dye_counterions}}$$

Figs. 7–9 present the dependencies of the surface charge density versus solution pH for the mixed oxide systems without and with dyes for their different concentrations (10, 20 and 30 mg/L).

As can be seen, the adsorption of the dyes causes increase of the solid surface charge and shift of pH_{pzc} (pzc—point of zero charge) toward higher values in relation to the system without dyes. The values of pH_{pzc} (at which the concentration of positively charged surface groups is the same as that of negatively charged ones) of all investigated suspensions are placed in Table 3. For comparison, the zero point charge of fly ash (43.7% silicon dioxide, 15.7%, aluminum oxide, 6.4% iron oxide, 9.8% calcium oxide and 0.9% magnesium oxide) was measured as 7.7, revealing that at $\text{pH} > \text{pH}_{\text{pzc}}$, the adsorption of the cationic dye such as methylene blue is favored [18]. According to Anbia and Salehi [30], the surface charge of amino functionalized silica strongly depend on solution pH and adsorption of C.I. Acid Blue 113, C.I. Acid Red 114, C.I. Acid Green 28, Acid Yellow 127 and Acid Orange 67 was reduced in the alkaline medium.

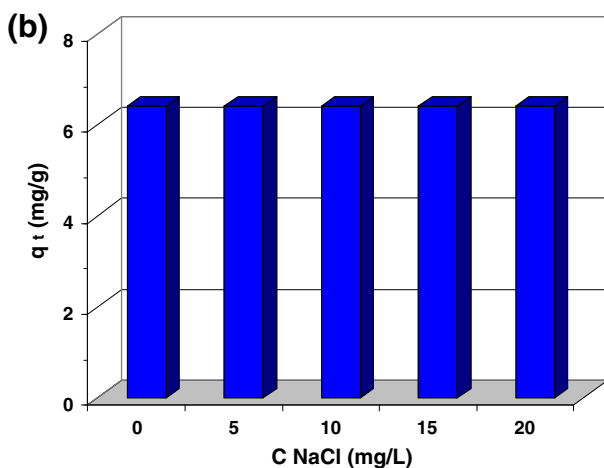
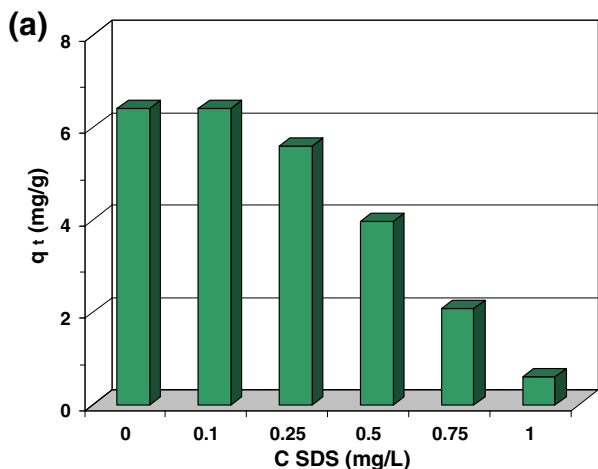


Fig. 6. Effect of the presence of (a) anionic surfactant and (b) sodium chloride on C.I. Direct Blue 71 sorption in the systems: 10 mg/L DB71 - 0.1–1 g/L SDS or 10 mg/L DB71 - 5–20 g/L NaCl, respectively.

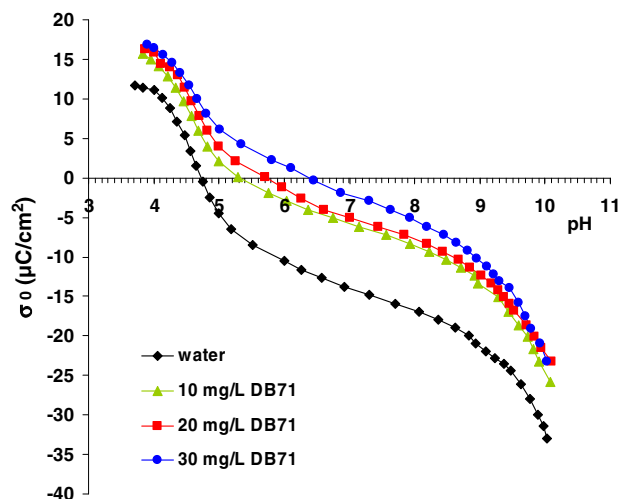


Fig. 7. Surface charge density of SA96 without and with C.I. Direct Blue 71 for different dye concentrations.

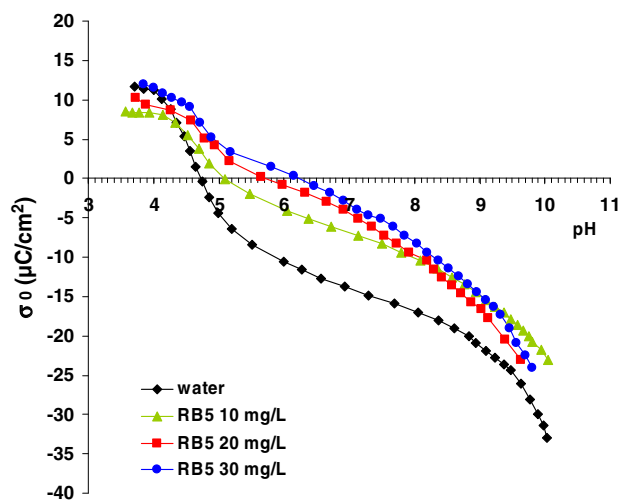


Fig. 8. Surface charge density of SA96 without and with C.I. Reactive Black 5 for different dye concentrations.

The adsorption of anionic dye containing negatively charged groups promotes the formation of a greater number of positive surface sites. It leads to increase of the solid surface charge in the dye presence. The higher the dye concentration, the more distinct the lowering of surface charge. It is rather obvious because in such cases the concentration of positively charged surface groups rises due to the electrostatic interaction with numerous functional groups of dye molecules.

The most pronounced difference between the surface charge of mixed oxide with dye and without it is observed for C.I. Direct Blue 71. This is most likely to be caused by the largest adsorption of C.I. Direct Blue 71 on the SA96 surface (capacity 49.2 mg/g) among all dyes. The smallest effect occurs for C.I. Acid Orange 7 (capacity 41.4 mg/g).

The addition of sodium chloride (as a supporting electrolyte) in the range 5–20 mg/L to the SA96–10 mg/L C.I. Direct Blue 71 systems results in noticeable lowering of the solid surface charge density in the pH range 4.4–8.3 (Fig. 10). On the other hand, in the pH range 8.3–10, the slight decrease of σ_0 is observed. Moreover, the electrolyte concentration practically does not influence the mixed oxide surface charge density in the dye presence (especially in the pH range 4.4–8). Such effect appears at higher pH values only for the system with the lowest NaCl concentration.

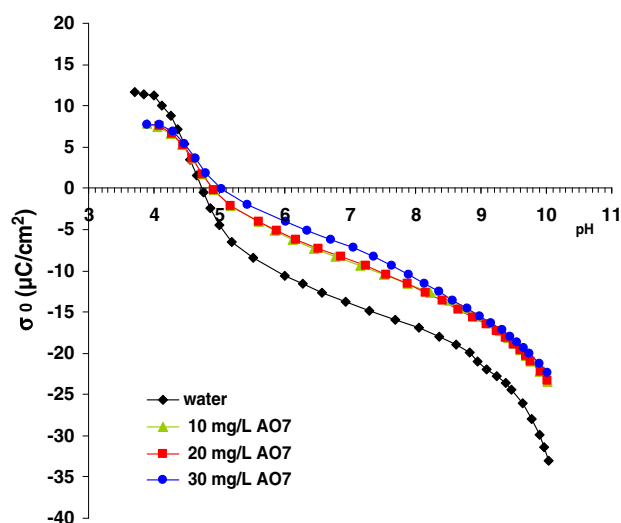


Fig. 9. Surface charge density of SA96 without and with C.I. Acid Orange 7 for different dye concentrations.

Table 3

pH_{pzc} of SA96 water systems in the absence and presence of the acid, reactive and direct dyes.

| System | Dye concentration (mg/L) | pH _{pzc} value |
|------------|--------------------------|-------------------------|
| SA96–water | 0 | 4.8 |
| SA96–DB71 | 10 | 5.3 |
| | 20 | 5.7 |
| | 30 | 6.4 |
| SA96–RB5 | 10 | 5.1 |
| | 20 | 5.7 |
| | 30 | 6.3 |
| SA96–AO7 | 10 | 4.9 |
| | 20 | 4.9 |
| | 30 | 5.0 |

The changes in the σ_0 values in the electrolyte presence result from the sodium chloride ions (Na^+ and Cl^-) adsorption in the surface layer. The lack of dependence of the solid surface charge density on the electrolyte concentration indicated that its lowest concentration (i.e., 5 g/L) ensures complete saturation of the surface active sites due to NaCl ions adsorption. Further increase of electrolyte concentration does not affect this composition of surface layer.

In contrast to sodium chloride, the presence of anionic surfactant exerted an effect on the surface charge density of the solid with the adsorbed dye. As can be seen in Fig. 11, the noticeable increase of the σ_0 of SA96–10 mg/L C.I. Direct Blue 71 system with the increasing SDS concentration is obtained (in relation to the system without surfactant). The higher the SDS concentration, the greater shift of pH_{pzc} in more alkaline values occurs (from pH 5.3 for the system without SDS to pH 9.1 for the system containing SDS with the highest concentration).

Taking into consideration the fact that C.I. Direct Blue 71 dye adsorption decreases with the increasing concentration of SDS, one can assume that surfactant molecules undergo preferential adsorption on the mixed oxide surface (in comparison to relatively large dye molecules). Its best proof is a significant increase of the solid surface charge density in the surfactant presence. Adsorbing surfactant molecules remove large dye molecules from the surface layer, contributing to the formation of a greater number of positively charged surface groups. As a result, the rise of σ_0 value of the studied systems containing SDS is observed.

The addition of the mixed silica–alumina to the examined wastewater sample changes considerably solid surface charge density—lowering of the σ_0 values in the whole studied pH range is observed (Fig. 12). Moreover, the solid surface charge density in the presence of

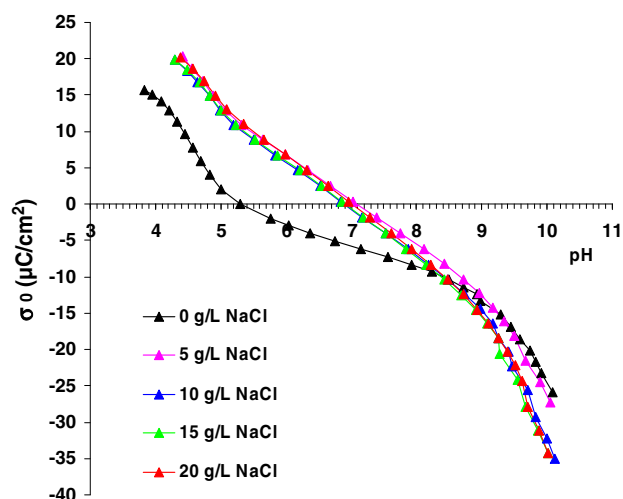


Fig. 10. Surface charge density of SA96 with C.I. Direct Blue B71 (10 mg/L) for different electrolyte concentrations.

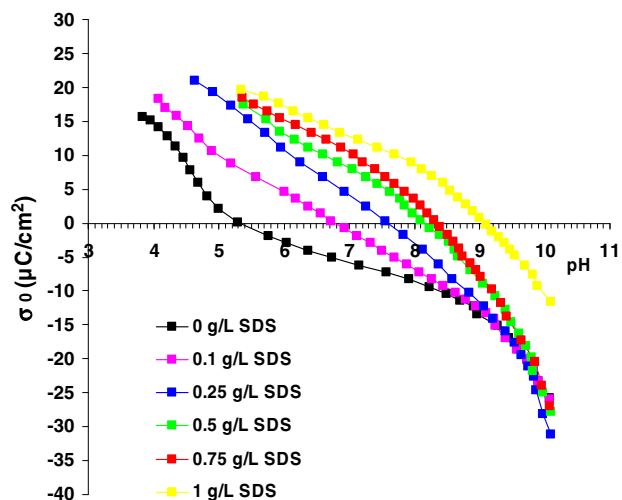


Fig. 11. Surface charge density of SA96 with C.I. Direct Blue 71 (10 mg/L) for different anionic surfactant concentrations.

wastewaters is negative and its density decreases from about $-7 \mu\text{C}/\text{cm}^2$ at pH 3.2 to about $-37 \mu\text{C}/\text{cm}^2$ at pH 6.2.

The negatively charged groups, belonging to different compounds making up the composition of the wastewaters, are probably responsible for lowering of the mixed oxide surface charge density. It should be emphasized that they are not groups directly bounded with the surface active sites, but those located in the surface layer together with different molecule fragments (which have no direct contact with the surface). The number of these unadsorbed groups must be much greater than the adsorbed ones, resulting in the reduction of the surface charge density of SA96.

4. Conclusions

The mixed oxide containing 4% SiO_2 and 96% Al_2O_3 (SA96) obtained by the CVD method was applied for removal of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 from aqueous solutions.

The pseudo second-order kinetic model described properly the experimental sorption data in the dye concentration range 10–30 mg/L. Of significant effect is the phase contact time on the values of the sorption capacities and decolorization of the raw textile wastewater. In the solutions containing 10–30 mg/L of C.I. Acid Orange 7 or C.I. Reactive Black 5, the dynamic equilibrium was reached after 180 min whereas

in the case of C.I. Direct Blue 71 aqueous solutions 240 min. Decolorization of the raw textile wastewater after the ozonation step on the level of 30% was achieved after 96 h. The experimental sorption capacities of SA96 toward the used dyes determined at equilibrium allowed to present the affinity series as follows: C. I. Direct Blue 71 > C. I. Reactive Black 5 > C. I. Acid Orange 7.

The mechanism of dye sorption on the mixed oxide is a miscellaneous interaction between the dye anions and the SA96, although a good correlation of the Langmuir isotherm model to the equilibrium sorption data was obtained. The effect of the presence of such auxiliaries as sodium chloride and anionic surfactant on the dye removal by SA96 was investigated, and it can be stated that a considerable decrease of q_e values was noticed with the increasing amount of SDS in the system. The adsorption of anionic dyes causes an increase of the SA96 surface charge density due to formation of an additional number of positive surface sites. Among all examined dyes, the most pronounced difference between the surface charge of mixed oxide with and without a dye is observed for C.I. Direct Blue 71 (exhibiting the largest adsorption). The addition of sodium chloride results in changes of the solid surface charge density, but the electrolyte concentration practically does not influence the σ_0 values of mixed oxide in the dye presence. Contrary, the presence of anionic surfactant causes a pronounced increase of the solid surface charge density with the adsorbed dye (preferential adsorption of SDS molecules in comparison to large C.I. Direct Blue 71 dye ones). The rich composition of wastewater sample makes that the surface charge of SA96 is significantly reduced compared to that obtained in water. The negatively charged groups of different wastewater compounds, but not directly bounded with the solid surface, are responsible for it.

Acknowledgment

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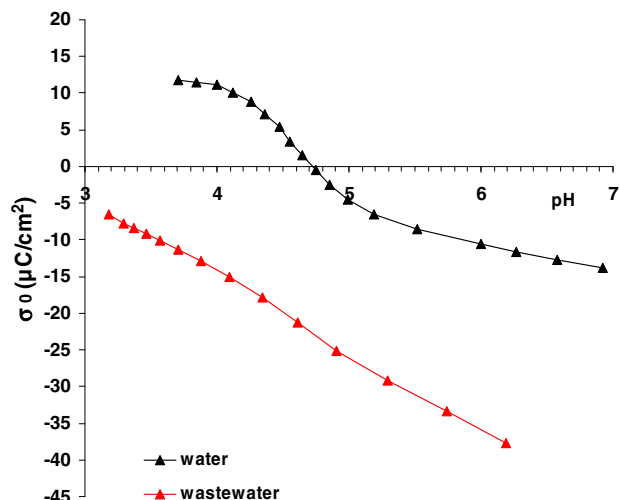


Fig. 12. Surface charge density of SA96 in the presence of raw wastewater.

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