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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% SiO_2 and 96% Al_2O_3 (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_t) 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.

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 worldwide 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 Eftekhar [10] evaluated the effectiveness of $Na_{0.5}Li_{0.5}CoO_2$ 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 $Na_{0.5}Li_{0.5}CoO_2$ 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-Fe_2O_3-Al_2O_3 amounting 498 mg/g was determined [12]. $Ni_{0.6}Fe_{2.4}O_4$ 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% SiO_2, 22.6% Al_2O_3) 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 TiO_2 to SiO_2 [19]. TiO_2–SiO_2 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.

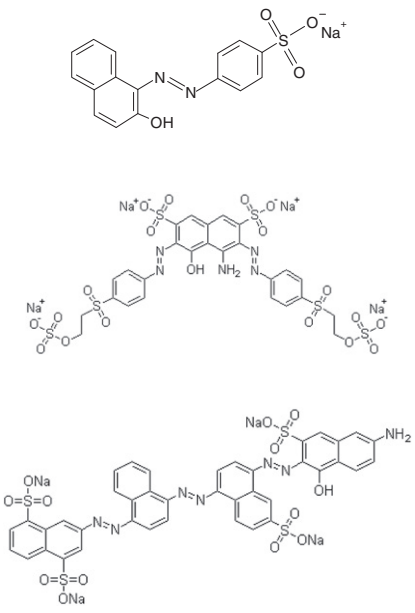
2. Experimental

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-(sulfooxy) 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-sulfonatonaphthalen-2(1H)-ylidene)hydrazino]-6-sulfonatonaphthalen-1-yl}diazenyl]naphthalen-1-yl}diazenyl]naphthalene-1,5-disulfonate) are presented in Fig. 1.

The samples of mixed alumina–silica oxide of the chemical composition: Al_2O_3 (96%) and SiO_2 (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 m^2/g and the mean pore diameter of 7.4 nm. Both parameters were determined by the low-temperature nitrogen adsorption–desorption isotherm method (Micrometritics ASAP 2405 analyzer, USA).



C.I. Acid Orange 7
C.I. No 15510
MW=350.32 g/mol

C.I. Reactive Black 5
C.I. No 20505
MW=991.82 g/mol

C.I. Direct Blue 71
C.I. No 34140
MW=1029.88 g/mol

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), Na_2CO_3, 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.