Zinc-titanium and cadmium-titanium nanocomposites as highly efficient photocatalysts in the destruction of pollutants in aqueous solutions

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ABSTRACT

Mesoporous zinc-titanium and cadmium-titanium powders were synthesized. Their structural, sorption and photocatalytic properties were studied. The photocatalytic active phase anatase was founded in all samples. Zinc containing samples demonstrate the presence of zincite phase. Dependence of pore volume, specific surface area and pore radii of amount of the said dopants was investigated. The characterization results of nitrogen adsorption-desorption measurements show that the obtained materials have type IV isotherms with H2 hysteresis loops. The composites showed higher photocatalytic and sorption activities as compared with pure titanium dioxide against dyes, surfactant and dichromate anion.   © 2015 Trade Science Inc. - INDIA

KEYWORDS

Titanium dioxide;
Cadmium;
Zincite;
Photocatalysis;
Composite.

INTRODUCTION

The bulk of waste waters containing dyes or surfactants are growing constantly. Various physic-chemical methods, namely chemical coagulation, precipitation, adsorption etc. are being used to treat sewage. Photocatalytic techniques are among the most perspective in this regard, because they allow one to mineralize organic pollutants completely or convert them into non-toxic state.

Oxides TiO_2, WO_3, ZnO, Fe_2O_3, SnO_2 etc. may be used as photocatalysts[1-5]. Titanium dioxide has the widest application. Its activation needs UV light (λd"387 nm). Unfortunately, a high recombination rate of electron–hole pairs in irradiated samples decreases the efficiency of this photocatalyst.

Currently the majority of works are devoted to synthesis of the TiO_2 samples having improved photocatalytic properties. Besides, it is important to prepare the materials with developed specific surface that conduces to concentrate pollutants on material surface with their following photocatalytic destruction.

A way to achieve this aim is synthesis of composite materials based on TiO_2. In this connection systems combining several semiconductors with various band gaps like TiO_2–WO_3[2, 3], TiO_2–MoO_3[5], TiO_2–SnO_2[3], and TiO_2–Fe_2O_3[4] are of great interest. These materials allow charge separation in higher yields and increase of their lifetime owing to

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possible interphase electron transfer.

In recent years, many works deal with preparation of modified TiO_2 samples having improved photocatalytic properties and higher specific surface which is favorable to pollutants adsorption on photocatalyst surface. Particular attention has been given to zinc oxide as titanium dioxide dopant[6-11]. This semiconductor has band gap width close to this value of titanium dioxide and also similar mechanism of photodestruction of various substances under UV irradiation. Lizama et al.[12] and Housková et al.[13] found also higher photocatalytic activity of ZnO as compared with TiO_2. Cadmium which may be adsorbed on titanium dioxide or introduced into its lattice is also used as dopant. Depending on doping method and dopant amount both negative[14, 15] and positive[16, 17] effects were observed.

The aim of our work was the preparation of nanosized titanium-zinc and titanium-cadmium composites having high specific surface, showing adsorption and photocatalytic activity to pollutants of different classes, as well as studying physic-chemical parameters of the obtained samples and establishing influence of adsorption properties on photocatalytic activity of titanium-zinc and titanium-cadmium composites.

MATERIAL AND METHODS

Composite preparation

Oxide titanium-zinc and titanium-cadmium nanocomposites were obtained through calcination of mixtures of titanium (IV) tetrabutoxide (Aldrich) (3g), citric acid (0.06 g), castor oil (2 ml) as well as ZnO or $CdCl_2$ (0.51 and 1.5 g, respectively). The obtained samples $1ZnO/TiO_2$, $2ZnO/TiO_2$, $3ZnO/TiO_2$ and $1Cd/TiO_2$, $2Cd/TiO_2$, and $3Cd/TiO_2$ were prepared by the annealing of mixture at 500°C during 2 h in the presence of air oxygen. Before annealing, mixture was carefully stirred to yield uniform mass. In addition, the TiO_2 sample was prepared using the above procedure without additions of ZnO or $CdCl_2$.

Photocatalysts characterization

X-ray phase analysis was performed using diffractometer Dron-4-07 (Russia) at CuK_α radiation (with copper anode and nickel filter) in reflection beam and the Bragg–Brentano registration geometry ($2\Theta = 10$–$70°$). Average crystallite size was determined using broadening of the most intensive band by means of the Debye–Scherer equation[18]: $D = 0.9\lambda/B\cdot\cos\Theta$, where 0.9 is constant, λ is wavelength, nm. Crystalline sizes were determined using the most intensive peaks characteristic.

Optical absorption spectra of powders were measured using the Perkin-Elmer Lambda Bio 35 spectrophotometer in the range between 200 and 1000 nm which allows one to convert data of corresponding spectra with the help of the Kubelka–Munk equation. The band gap value (E_g) was calculated according to[19] using the following formula: $E_g = 1239.8/\lambda$ where λ (nm) is wavelength of spectrum origin.

The values of specific surface (S_{sp}) of the samples as well as distribution of pores by volume were determined using Quantachrom NovaWin2 device. The specific surface of the samples was determined from isotherms of nitrogen sorption-desorption using the Brunauer–Emmet–Teller (BET) approach[20]. The pore radius (R) and the pore volume (V_{tot}) were calculated from the desorption branches of the isotherms using the Barret–Joiner–Halenda method[21].

Photocatalytical experiment

Photocatalytic activity of samples was evaluated by rate constants of destruction (k_d) of several model pollutants. These were cationic dyes safranine T (*SF*) (C = 0.03 g/l) and methylene blue (*MB*) (C = 0.03 g/l), anionic dye tetrachlorofluoresceine (*TCF*) (C = 0.09 g/l), cationic surfactant tetradecylpiridinium chloride (*TDPC*) (C = 0.09 g/l), as well as potassium dichromate (*PD*). In particular, dichromate anions are highly toxic and carcinogenic pollutants contributed by industrial processes like electroplating chemical processes, dye production, leather tanning. The reduction of Cr (VI) to Cr (III) is favorable to decrease toxicity, as well as to precipitation of chromium compounds in basic mediums.

Before irradiation, catalyst suspension (2 g/l) in aqueous substrate solution was left to stand in dark

up to achieve adsorption equilibrium.

The irradiation of aqueous solutions of dyes, surfactant and dichromate anion was performed using low pressure UV lamp BUV-30 (Ukraine) with power of 30 W in quartz reactor in the presence of air oxygen.

Concentrations of the substrates were measured spectrophometrically in the course of experiment using Shimadzu UV-2450 spectrophotometer at $\lambda = 520$ nm for *SF*, $\lambda = 610$ for *MB*, $\lambda = 510$ nm for *TCF*, $\lambda = 260$ nm for *TDPC* and $\lambda = 350$ nm for dichromate anion. Photocatalytic rate constants for the model compounds were calculated using the first order kinetic equation.

RESULTS AND DISCUSSION

Crystalline structure of the samples was investigated using X-ray phase method (Figure 1). The study of diffraction patterns and corresponding 2Θ values for diffraction peaks proved the presence of anatase phase in all the samples. Thus, diffractogram of titanium dioxide sample shows intensive peaks $2\Theta = 25.5, 37.8, 40.0, 54.0$ and 55.0 which belong to anatase phase (Figure 1, a). The same phase was detected for the composite samples. Our samples show peaks $2\Theta = 27.4, 41.2$ which belong to rutile phase. This result is in contradiction with the works by Antonelli et al. and Kim et al.[22, 23] who allege that various additives prevent the anatase–rutile phase transition during titanium dioxide production.

Diffraction peaks intrinsic for rutile are more intensive for zinc- and cadmium-containing materials (Figure 1, b, and c). Our results agree with the data of Xu et al. and Smirnova et al.[24, 25] who found that Cd, Au, Mn and Ag additives promote the crystallization of powders and assist the anatase–rutile transition. Rutile phase in zinc- and cadmium-containing samples was also found by Andronis et al., Housková et al., and Ptashko et al.[16, 26, 27]. It was found that zincite phase (ZnO) with $2\Theta = 36.2, 56.6$ (Figure 1, b) is present in the zinc-containing materials. This agrees with the data obtained by the authors[6].

Absorption bands of the composites were blue shifted compared to pure TiO_2. This result indicates that the distribution of zinc oxide in the ZnO/TiO_2

composite is uniform and also corresponds to literature data[6, 27]. The largest shift is observed for powder with the highest zincite content.

In contrast to the work[9] we had not found intensive peaks characteristic of zinc titanates. Cadmium titanate phase is present in cadmium-containing samples ($2Cd/TiO_2$, $3Cd/TiO_2$). This phase had been found also in work[16].
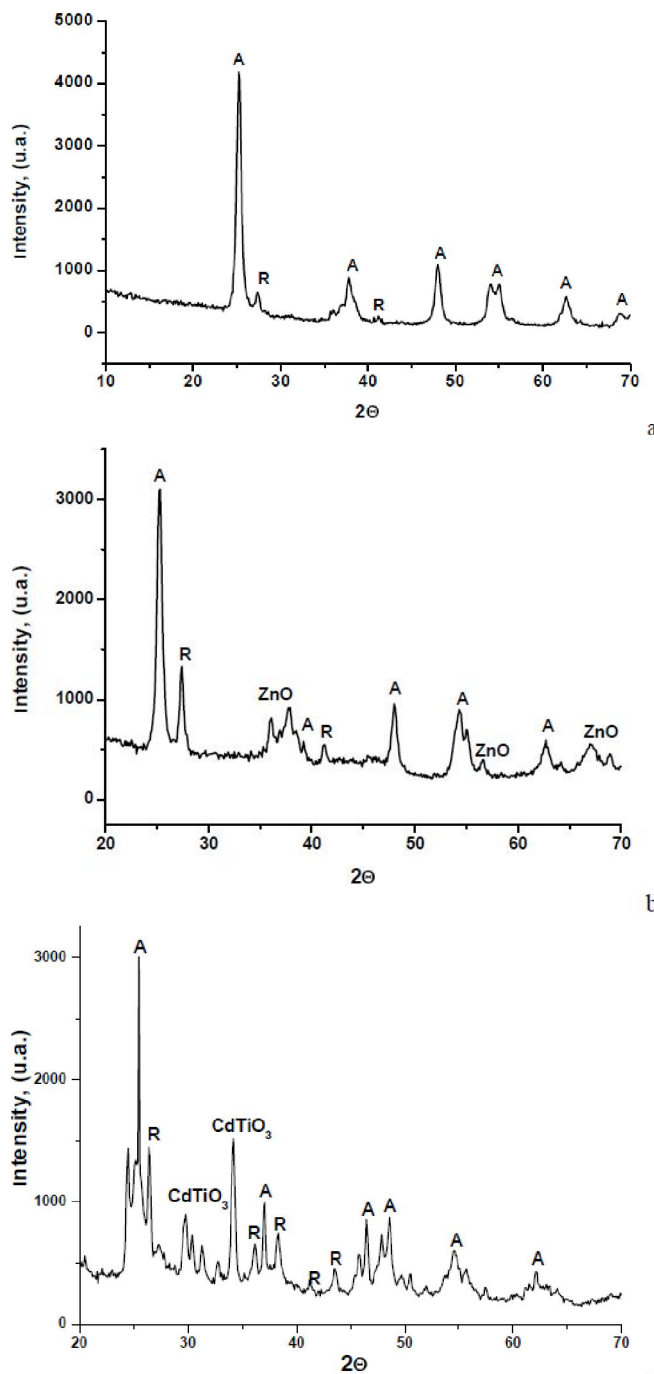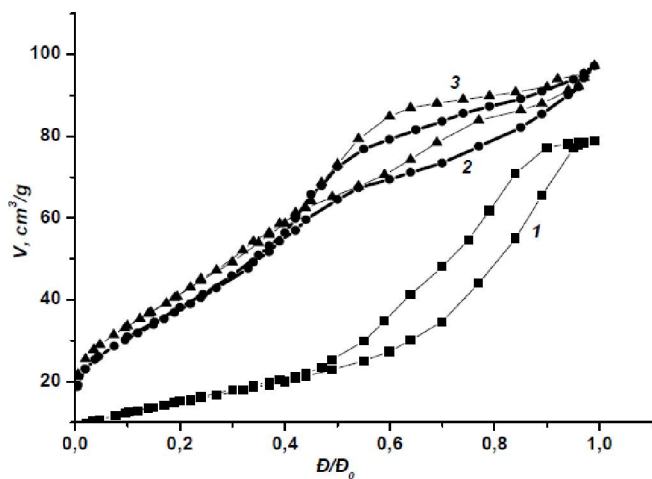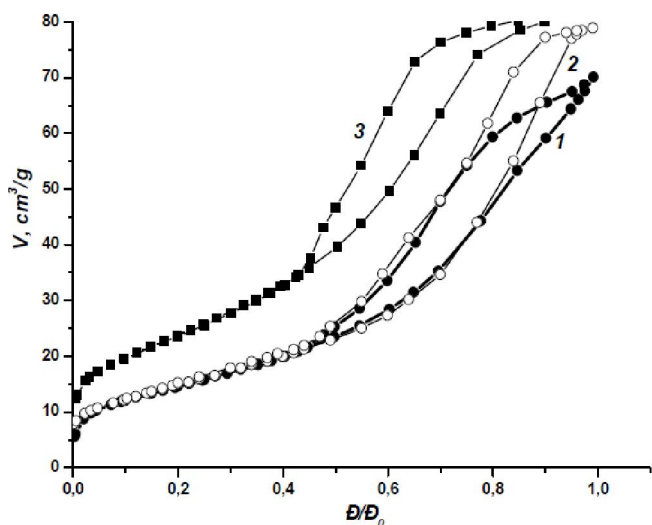

Figure 1 : X-ray patterns: TiO_2 (a), $2ZnO/TiO_2$ (b), $2Cd/TiO_2$ (c)
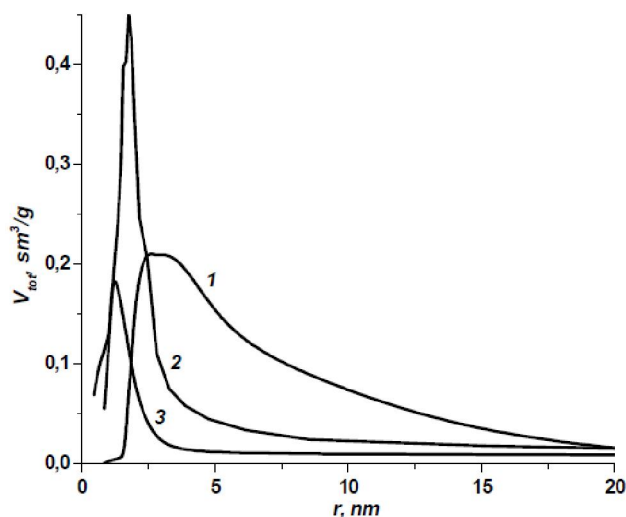
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a

b

Figure 2 : Isotherms of nitrogen sorption-desorption obtained at 20⁰c for samples: a - *1* - TiO₂; *2* - 2ZnO/TiO₂; *3* - 3ZnO/TiO₂, a - *1*- 2Cd/TiO₂, 2 - б , *3* - 1Cd/TiO₂

a

b

Figure 3 : Pore size distribution for the obtained samples: a: *1* – TiO₂, 2 – 1ZnO/TiO2, *3* - 3ZnO/TiO₂; б : *1*- TiO₂, 2 – 2Cd/TiO₂, *3* - 3Cd/TiO₂)
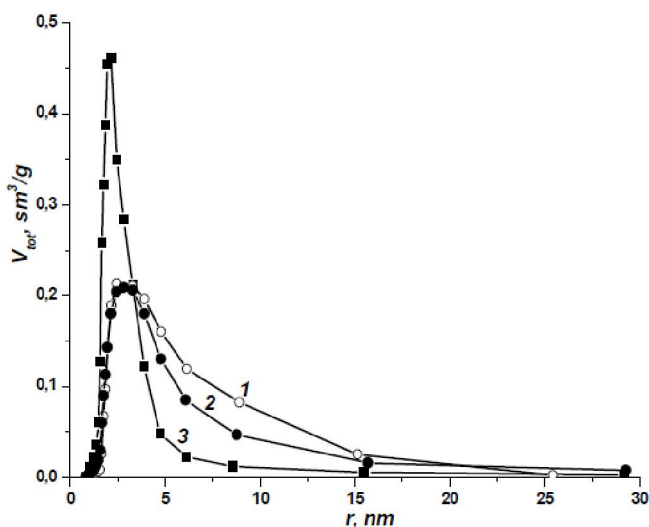
Crystallite size in agglomerates of titanium dioxide calculated with the help of Debye–Scherer equation are 9.5 nm. Their value increases up to 10–11 nm in the case of composite samples, because the presence of modificators accelerates titanium dioxide crystallization and increases crystallite size. That is consistent with the literature data[26]. The size of zincite crystallites is 10.1 nm.

The study of nitrogen sorption–desorption isotherms at 20°C for the synthesized samples demonstrated that the obtained materials have type IV isotherms with H2 hysteresis loops in all the cases (Figure 2) that indicates mesoporous powder structure[28].

The area of size pore distribution shifts to smaller values as zincite and cadmium amount in the samples increases (Figure 3).

In contrast with[26] our samples have higher specific area, pore radius and pore volume (TABLE 1).

Specific surface of composite samples increases in 1.5–2.5 times as compared with pure titanium dioxide. The 2ZnO/TiO₂ and 3ZnO/TiO₂ samples are characterized by the highest S_{sp}. The presence of zincite in the samples favours further pore growth from 0.12 to 0.15 cm³/g. In the case of cadmium-containing samples pore volume is almost the same. The average pore radius for modified samples decreases as compared with pure titanium dioxide (4.87

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TABLE 1 : Samples characteristics

Sample	S_{sp}, m²/g	R, nm	V_{tot}, cm³/g	E_g, eV
TiO₂	50	4.87	0.12	3.45
1 ZnO/TiO₂	80	3.53	0.14	3.35
2 ZnO/TiO₂	127	2.36	0.15	3.42
3 ZnO/TiO₂	139	2.16	0.15	3.46
1 Cd/TiO₂	94	4.13	0.12	3.38
2 Cd /TiO₂	71	4.36	0.11	3.43
3 Cd /TiO₂	86	4.1	0.11	3.39

TABLE 2 : Rate constants of photocatalytic destruction ($k_d \times 10^3$, s⁻¹) and sorption values (a, %) of the investigated substances

Substrate	SF		MB		TCF		TDPC		PD	
Photocatalyst	k_d	a	k_d	a	k_d	a	k_d	a	k_d	a
—	0.03	—	0.06	—	0.61	—	0.09	—	0.09	—
TiO₂	0.11	76.5	0.20	71.4	0.83	64.7	0.12	23.0	0.12	23.0
ZnO	0.04	3.00	0.03	11.0	0.80	2.00	0.10	2.00	0.10	2.00
1ZnO/TiO₂	0.47	38.5	0.44	29.3	2.71	34.0	0.26	38.0	0.26	38.0
2ZnO/TiO₂	0.92	63.27	1.38	66.5	1.37	31.3	0.16	26.0	0.16	26.0
3Zn/TiO₂	0.65	52.4	0.21	18.8	3.14	43.9	0.36	45.0	0.36	45.0

nm): for zinc-containing samples it equals to 2.16 nm and for cadmium containing samples to 4.1 nm.
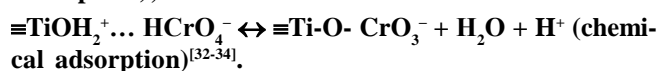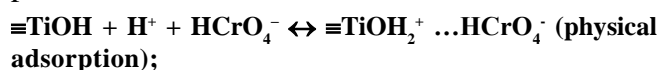
The band gap value of all modified samples is close to the value typical for pure titanium dioxide (TABLE 1). Dopant amount does not affect gap values.

Sorption equilibrium in the photocatalyst–substrate system is established within 1 hour for the case of dichromate anion and TDPC, within 2 hours for SF and MB, and within 0.5 hour for TCF. The highest adsorption activity was found for titanium dioxide sample in spite of the smallest specific surface. This can be connected with the presence of the pores with the highest radii (TABLE 1) which take part in adsorption process.

Irradiation of aqueous solutions of dyes and surfactants was performed at neutral pH, whereas photocatalytic reduction of dichromate anion was performed at acid pH. The value of pH=2 was selected according to the results obtained by Hongxiang et al.[29] who showed that the adsorption of Cr (VI) ions on titanium dioxide surface decreases as a result of pH increasing that is explained by changing of the adsorption ability in the series of various Cr(VI) ion forms (dichromate ion–hydrochromate–chromate ion) at different pH on TiO₂ surface. Moreover, pH

change affects physic-chemical properties of photocatalyst surface. According to Fujishima et al. and Hoffmann et al.[30, 31] isoelectric point of titanium dioxide is situated at pH=6–6.5. At pH below this value titanium dioxide surface is charged positively which is favourable for $Cr_2O_7^{2-}$ anion adsorption, while increase of pH leads to negative charge of titanium dioxide surface, resulting in decrease of anion adsorption.

Rodenas et al.[32] showed that $Cr_2O_7^{2-}$ anion can be chemisorbed on titanium dioxide surface. The main adsorption centers are protonated hydroxyl groups of titanium dioxide surface and non-dissociated surface hydroxyl groups. The scheme of adsorption equilibrium in the system potassium dichromate solution–titanium dioxide in acid medium can be presented as follows:

$\equiv$**TiOH + H⁺ + HCrO₄⁻ $\leftrightarrow$ $\equiv$TiOH₂⁺ …HCrO₄⁻ (physical adsorption);**

$\equiv$**TiOH₂⁺… HCrO₄⁻ $\leftrightarrow$ $\equiv$Ti-O- CrO₃⁻ + H₂O + H⁺ (chemical adsorption)**[32-34].

The UV irradiation of the aqueous solutions of MB, SF and potassium dichromate by PRK-1000 lamp without photocatalyst does not change essentially their absorption spectra. In the case of TCF dye concentration decrease was observed, but com-

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TABLE 3 : Rate constants of photocatalytic destruction ($k_d \times 10^3$, s^{-1}) and sorption values (a, %) of the investigated substances

Substrate	SF		MB		TCF		TDPC		PD	
Sample	k_d	a	k_d	a	k_d	a	k_d	a	k_d	a
—	0.03	—	0.06	—	0.61	—	0.09	—	0.09	—
TiO_2	0.11	76.5	0.20	71.4	0.83	64.7	0.12	23.0	0.12	23.0
$1Cd/TiO_2$	0.81	63.8	0.48	20.6	1.38	74.7	0.22	7.86	0.22	7.90
$2Cd/TiO_2$	0.77	55.6	0.59	40.0	1.45	94.4	0.26	8.60	0.23	15.6
$3Cd/TiO_2$	0.60	50.3	0.24	12.2	0.74	89.3	0.17	3.00	0.17	15.0

plete destruction did not occur. The presence of photocatalyst during irradiation results in complete dye destruction and transformation of Cr (VI) into Cr (III). Thus, aqueous $K_2Cr_2O_7$ solutions being irradiated show decreasing absorption band of dichromate ion at 350 nm and emergence of a new band at 550 nm which is characteristic for Cr (III) ions. Reaction rates of photoreduction and photodestruction depend on the composition and structure of photocatalysts (TABLES 2 and 3).

As opposite to works[12, 13] TiO_2 in these reactions demonstrated higher photoactivity as compared to zinc oxide (TABLE 2), although the authors of paper[7] found higher zinc oxide activity in the reaction of methyl orange photodestruction.

In all the cases composite samples demonstrated higher photocatalytic activity (TABLES 2 and 3). This agrees with the results of the authors[9–11, 16, 17 and 35].

Increase of the photocatalytic activity of the composites was explained by the authors[11] through interaction between ZnO and TiO_2. They argue that chemical interaction between ZnO and TiO_2 in the form of the Zn–O–Ti bond may affect the photoefficiency of binary oxide catalysts.

Enhanced photocatalytic activity for these materials as compared with pure oxides can also be explained by both the rise of specific surface and the appearance of new types of acid centers[35] which can favour substrate adsorption on photocatalyst surface. One can see from TABLES 2 and 3 that the rate constants of photoreactions increase with increasing amount of adsorbed substance. The highest photocatalytic ability in the reactions of SF and MB destruction was demonstrated by $2ZnO/TiO_2$ sample. The $3ZnO/TiO_2$ sample was more active in the reactions of dichromate anion photoreduction and of

TCF and TDPC oxidation. In all cases values of k_d and adsorption correlate which is the evidence that the molecules adsorbed on powder undergo photocatalytic destruction (TABLE 2).

Of all the cadmium-containing samples $1Cd/TiO_2$ sample demonstrated the highest photocatalytic ability in the reactions of CF destruction, while $2Cd/TiO_2$ sample was more active in other cases.

In the case of anionic TCF dye the highest adsorption activity was shown by cadmium-containing samples that can be connected with their structure characteristics (TABLE 1).

Dichromate anion and TDPC are better adsorbed on zinc-containing samples among which the $3Zn/TiO_2$ sample was the most active that can be connected with the emergence of new acid adsorption centers on the surface of zinc-containing composites[27]. In all the cases zincite showed the lowest adsorption activity. Comparing the activity of all the composites under study one can see that zinc-containing samples are more active in all the investigated reactions.

Increase of k_d for composite materials as compared to pure oxides is connected not only with the enhancement of specific surface and with the appearance of acid centers of new type that are favourable for adsorption and further destruction of adsorbed molecules, but also with the fact that charge separation during UV irradiation can increase on interface boundaries between TiO_2 and ZnO phases as well as between TiO_2 and cadmium-containing phase.

CONCLUSIONS

Zinc and cadmium-containing composite mate-

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rials based on titanium dioxide were synthesized, their specific surface being higher than that of pure TiO_2. X-ray analysis supported the presence of anatase in all the synthesized samples as well as of zincite phase in zinc-containing composites. Composite materials demonstrated high photocatalytic and adsorption activity relative to dyes, surfactant and dichromate anion which is connected with increasing specific surface and emergence of acid centers of new type[35]. In addition, interaction between TiO_2 and ZnO phases as well as between TiO_2 and cadmium-containing phase can increase charge separation on UV irradiation[11]. The rate constants of photocatalytic reactions increase as the amount of adsorbed substrate increases. This fact points out that adsorbed molecules react first.

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