

ISSN: 3093-9305

VOLUME - 4

# JOURNAL OF GLOBAL SCIENTIFIC INNOVATIONS





**Shurtan gaz-kimyo majmuasining ishlatilgan titan dioksidi katalizatorini ZnPc/Fe bilan modifikatsiyalangan sorbent–fotokatalizatorlarga qayta ishlash: sintez va eksperimental metodologiya**

**A. O. Toshpo'latov** ([toshpolatova018@gmail.com](mailto:toshpolatova018@gmail.com))

*<sup>1</sup>Toshkent kimyo-texnologiya instituti, Kimyo muhandisligi texnologiyasi fakulteti*

**R. M. Abdunazarova** ([oabdulloh38@gmail.com](mailto:oabdulloh38@gmail.com))

*<sup>2</sup>Nizomiy nomidagi O'zbekiston Milliy pedagogika universiteti*

**Annotatsiya.** Ushbu maqolada Shurtan gaz-kimyo majmuasi (Sh.G.K.M.) tomonidan chiqarib tashlanadigan ishlatilgan titan dioksidi katalizatorini suvdagi barqaror organik bo'yoqlarning foto-Fenton parchalanishi uchun mo'ljallangan geterogen sorbent–fotokatalizator materiallariga aylantirish bo'yicha to'liq eksperimental protokol tavsiflangan. Ishlatilgan katalizator adsorblangan organik qoldiqlarni yo'qotish uchun 500–650 °C haroratda termik faollashtirildi, so'ngra TiO<sub>2</sub>-Fe va TiO<sub>2</sub>-ZnPc kompozit materiallarini olish maqsadida ketma-ket temir oksidi va rux ftalotsianini (ZnPc) bilan singdirildi. Model ifloslantiruvchi sifatida metilen ko'k (MK) dan foydalangan holda partiyali sorbtsiya–fotoparchalanish protokoli reagentlarning tozaligi, asboblar, nurlantirish sharoitlari, namuna olish jadvali hamda UV-Vis yutilish ma'lumotlaridan sorbtsiya sig'imi va tashqi tezlik konstantalarini aniqlash uchun ishlatilgan kinetik tenglamalar bilan birga to'liq eksperimental tafsilotda keltirilgan. Ushbu metodologiya qayta ishlangan katalizatorlar asosidagi foto-Fenton tizimlarini baholash uchun takrorlanuvchan asos bo'lib xizmat qiladi va ushbu seriyaning keyingi tavsiflash hamda samaradorlik tadqiqotlari uchun ma'lumotnoma protokol sifatida mo'ljallangan.

**Kalit so'zlar:** ishlatilgan katalizatorni qayta ishlash; TiO<sub>2</sub> ni faollashtirish; rux ftalotsianini; temir oksidi bilan singdirish; sorbtsiya kinetikasi; metilen ko'k; eksperimental metodologiya.

**Переработка отработанного катализатора диоксида титана Шуртанского газохимического комплекса в сорбенты-фотокатализаторы, модифицированные ZnPc/Fe: синтез и экспериментальная методология**

**Аннотация.** В данной статье представлен полный экспериментальный протокол переработки отработанного катализатора диоксида титана, выбрасываемого Шуртанским газохимическим комплексом (Ш.Г.Х.К.), в гетерогенные сорбенты-фотокатализаторы, предназначенные для фото-Фентон деградации устойчивых органических красителей в воде. Отработанный катализатор подвергался термической реактивации при 500–650 °C для удаления адсорбированных органических остатков, после чего последовательно пропитывался оксидом железа и цинковым фталоцианином



(ZnPc) для получения композитных материалов  $\text{TiO}_2\text{-Fe}$  и  $\text{TiO}_2\text{-ZnPc}$ . Периодический протокол сорбции-фотодеградации с использованием метиленового синего (МС) в качестве модельного загрязнителя представлен в полном экспериментальном объеме, включая чистоту реагентов, приборное обеспечение, условия облучения, график отбора проб и кинетические уравнения, применяемые для определения сорбционной ёмкости и кажущихся констант скорости по данным УФ-видимой абсорбции. Представленная методология обеспечивает воспроизводимую основу для оценки систем фото-Фентон на основе переработанных катализаторов и предназначена в качестве эталонного протокола для последующих исследований характеристики и эффективности.

**Ключевые слова:** переработка отработанного катализатора; реактивация  $\text{TiO}_2$ ; цинковый фталоцианин; пропитка оксидом железа; кинетика сорбции; метиленовый синий; экспериментальная методология.

### **Recycling of Spent Titanium Dioxide Catalyst from the Shurtan Gas-Chemical Complex into ZnPc/Fe-Modified Sorbent–Photocatalysts: Synthesis and Experimental Methodology**

**Abstract.** This paper describes a complete experimental protocol for converting spent titanium dioxide catalyst discarded by the Shurtan Gas-Chemical Complex (Sh.G.C.C.) into heterogeneous sorbent–photocatalyst materials suitable for the photo-Fenton degradation of persistent organic dyes in water. The spent catalyst was thermally reactivated at 500–650 °C to remove adsorbed organic residues, then sequentially impregnated with iron oxide and zinc phthalocyanine (ZnPc) to obtain  $\text{TiO}_2\text{-Fe}$  and  $\text{TiO}_2\text{-ZnPc}$  composite materials. A batch sorption–photodegradation protocol using methylene blue (MB) as a model pollutant is presented in full experimental detail, including reagent purity, instrumentation, irradiation conditions, sampling schedule and the kinetic equations used to extract sorption capacity and apparent rate constants from the UV-Vis absorbance data. The methodology reported here provides a reproducible basis for evaluating recycled-catalyst photo-Fenton systems and is intended as a reference protocol for subsequent characterization and performance studies.

**Keywords:** spent catalyst recycling;  $\text{TiO}_2$  reactivation; zinc phthalocyanine; iron oxide impregnation; sorption kinetics; methylene blue; experimental methodology.

## **INTRODUCTION**

Large-scale industrial gas-purification operations, such as those carried out at the Shurtan Gas-Chemical Complex (Sh.G.C.C.) in Uzbekistan, employ titanium-containing catalysts that gradually lose activity through surface fouling with organic and sulfur-containing residues and are subsequently discarded as solid waste. Rather than treating this spent material as a disposal liability, it can be reactivated and re-



purposed as an inexpensive feedstock for heterogeneous photocatalysts and sorbents used in wastewater treatment. This paper reports, in full experimental detail, the methodology developed for (i) reactivating the spent Sh.G.C.C. titanium dioxide catalyst, (ii) modifying it with iron oxide and zinc phthalocyanine (ZnPc) to impart photo-Fenton and visible-light-sensitized photocatalytic activity, and (iii) evaluating its sorption and photodegradation performance toward the model cationic dye methylene blue (MB).

## MATERIALS

All experiments were carried out using reagents of 'pure' and 'chemically pure' grade. Precise quantities of metal salts, in particular iron nitrate, were dissolved in a fixed volume of acidified aqueous medium to prepare stock solutions with minimized concentration error. Distilled water was used as the principal solvent throughout, and a set of 'pure'-grade reference solvents (ethanol, acetone and other organic liquids) was used to control reaction media and to assess the solubility behaviour of the synthesized materials. Methylene blue (MC/MB) was used as the model organic pollutant for sorption and photodegradation experiments.

The elemental (metal) composition of the raw and processed catalyst was determined by inductively coupled plasma optical emission spectrometry (ICAP Pro ICP-OES, Thermo Fisher, USA); carbon, hydrogen, sulfur and nitrogen content was determined using a FlashSmart elemental analyzer. Thermal behaviour was studied by simultaneous thermal analysis (STD 450, TA Instruments, USA) at a heating rate of 9 °C/min using 6–7 mg sample masses, recording TG, DTG and DTA signals. Surface microstructure was examined using a JEOL IT-200 scanning electron microscope (Japan). Phase composition was determined by X-ray diffraction using a Shimadzu XRD-6100 diffractometer (Japan).

## SYNTHESIS OF SORBENT-PHOTOCATALYST MATERIALS

### *Reactivation of the spent Sh.G.C.C. titanium dioxide catalyst*

The spent titanium dioxide catalyst recovered from the Shurtan Gas-Chemical Complex was calcined in a muffle furnace at 650 °C to remove residual organic compounds accumulated during its service life in the plant. The resulting powder was dried and subsequently used as the base photocatalyst for the photodegradation of organic dyes under ultraviolet irradiation.



Figure 1. Photographs of the recycled titanium dioxide materials: (a) the spent Sh.G.C.C. TiO<sub>2</sub> catalyst prior to calcination, (b) iron-oxide-impregnated



titanium dioxide (TiO<sub>2</sub>-Fe), and (c) zinc phthalocyanine-modified titanium dioxide (TiO<sub>2</sub>-ZnPc).

The particle size of the as-received spent catalyst granules was approximately 1.5 mm in diameter; prior to impregnation with ZnPc and prior to sorption experiments, the spent catalyst was sieved to a controlled particle-size fraction. To remove loosely bound surface contaminants before impregnation, 50 g of the spent titanium catalyst was suspended in a 1:1 (v/v) ethanol–water solution and stirred magnetically for 2 hours. The suspension was then filtered, the solid rinsed with deionized water (18.2 MΩ·cm, Thermo Fisher purification system) and dried at 100 °C for 1 hour before proceeding to the iron oxide and ZnPc impregnation steps.

#### ***Development of the aqueous sorption and photocatalytic oxidation procedure***

The photocatalytic performance of the synthesized materials was evaluated using methylene blue (MB) as a representative organic pollutant. Photodegradation experiments were performed in a 60 mL glass tubular reactor under visible-light irradiation supplied by a 400 W tungsten-halogen lamp. The reaction temperature was maintained at 25 °C by circulating water through the reactor's cooling jacket. The initial MB concentration in the aqueous solution was 10 mg L<sup>-1</sup>, and the mass of photocatalyst sample used was 50 mg. In each run, the photocatalyst was first dispersed in 50 mL of the 10 mg L<sup>-1</sup> MB solution in a glass vial and the suspension stirred in the dark for 2 hours to establish adsorption–desorption equilibrium prior to irradiation.

During the photodegradation reaction, 2 mL aliquots of the suspension were withdrawn at defined time intervals for subsequent analysis. The residual MB concentration in each aliquot was determined using a Duetta UV-Vis spectrophotometer (Horiba, Japan). In a parallel series of experiments designed to evaluate photo-Fenton-type behaviour, 0.1 mL of H<sub>2</sub>O<sub>2</sub> was introduced into the reaction system under otherwise identical conditions.

The sorption efficiency of each material was calculated using Equation (1):

$$\text{Sorption (\%)} = [(C_i - C_e) / C_i] \times 100 \quad (1)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium (final) concentrations of the dye (mmol L<sup>-1</sup>), respectively.

Dark-adsorption experiments were performed by mixing photocatalyst powder (1.0 g/L) with MB ( $3 \times 10^{-5}$  M) in an ascorbic-acid or oxalic-acid buffer solution (0.01 M) at pH 3.3. Preliminary experiments carried out over 6 hours under continuous stirring showed that equilibrium was reached after approximately 2 hours; measurements in the present study were therefore always initiated 2 hours after the start of the dark adsorption period. Photocatalytic runs were then carried out in a 100 mL reactor containing the  $3 \times 10^{-5}$  M MB / 0.01 M ascorbic-acid solution and 0.1 g of catalyst powder, at room temperature (25 °C) under constant stirring. A negative control without catalyst was run in parallel for every experiment. Unless the effect of pH itself was under investigation, all reaction systems were maintained at pH 3.3; where pH was varied, this was achieved by adjusting the ratio of ascorbic acid to



sodium ascorbate in the buffer, whose capacity maintained the target pH throughout each run.



**Figure 2. Visual progression of the photocatalytic decolorization of the methylene blue solution under irradiation, recorded at 0, 5, 15, 30, 60, 90 and 180 minutes.**

As shown by the sequence of solutions in Figure 2 and by the corresponding UV-Vis absorption spectra recorded in parallel, the intensity of the characteristic MB absorption band decreases progressively over the 180-minute irradiation period, and prolonged irradiation under pH control leads to near-complete decolorization of the dye solution - direct visual and spectroscopic evidence of dye degradation.

#### ***Kinetic treatment of the photodegradation data***

The apparent rate constant ( $k$ ) of dye photodegradation was extracted from the experimental data using the Langmuir–Hinshelwood kinetic model, applied in its pseudo-first-order form. A good linear relationship between  $\ln(C/C_0)$  and irradiation time ( $t$ ) is typically observed during the first 20–30 minutes of UV exposure, where  $C_0$  is the initial dye concentration; the apparent rate constant is obtained as the slope of this linear region. Although several concurrent mechanisms may contribute to the overall dye transformation - surface adsorption, homogeneous or heterogeneous oxidation, and direct photolysis of reaction intermediates among them - the relative contribution of each pathway is not always fully resolved, and the pseudo-first-order treatment is used here as a practical means of comparing the photocatalytic activity of different recycled-catalyst formulations.

| Parameter                | Value                                                         |
|--------------------------|---------------------------------------------------------------|
| Reactor volume           | 60 mL (100 mL for adsorption/pH studies)                      |
| Light source             | 400 W tungsten-halogen lamp (visible light)                   |
| Reaction temperature     | 25 °C (water-jacketed cooling)                                |
| Initial MB concentration | 10 mg L <sup>-1</sup> ( $3 \times 10^{-5}$ M in kinetic runs) |
| Catalyst dose            | 50 mg per 50 mL (1.0 g L <sup>-1</sup> in adsorption runs)    |
| Dark equilibration time  | 2 h                                                           |
| Working pH               | 3.3 (ascorbic acid / sodium ascorbate buffer)                 |
| Analytical method        | UV-Vis spectrophotometry (Duetta, Horiba, Japan)              |



**Table 1. Summary of the standard experimental conditions used for sorption and photodegradation runs.**

### PHASE ANALYSIS BY X-RAY DIFFRACTION

The phase composition of the starting materials and of the obtained sorbents is a key factor governing sorption and photocatalytic efficiency. Experimental diffraction patterns of the starting materials and derived sorbents show the presence of an amorphous phase (characterized by broad, diffuse peaks) together with several crystalline phases, consistent with literature data on the phase composition of inorganic slag-type components.

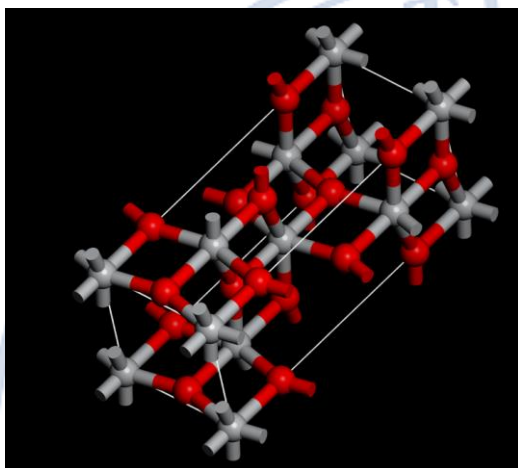


**Figure 3a. Crystal model of the anatase polymorph of titanium dioxide used as a reference for diffraction-pattern identification.**

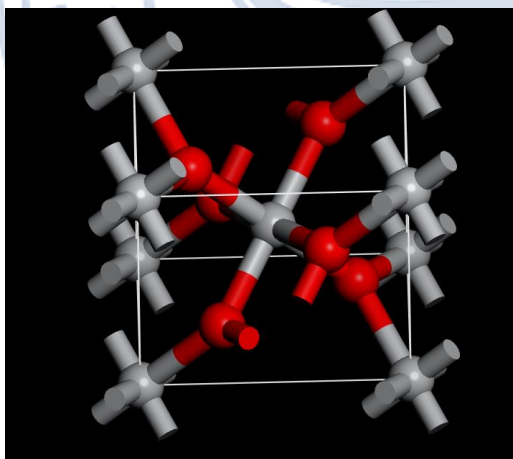


**Figure 3b. Crystal model of the rutile polymorph of titanium dioxide used as a reference for diffraction-pattern identification.**

Identification of the crystalline phases present in the sorbent series was performed by X-ray line-profile analysis using the MDI Jade software package (version 5.0) in conjunction with the JCPDS-PDF2 (2004) powder-diffraction reference database, which enables quantitative and qualitative phase analysis as well as calculation of theoretical diffraction patterns. This database comprises 54 sub-databases spanning inorganic compounds, organic compounds, minerals, alloys,



semiconductors, corrosion phases, zeolites, pigments, polymers, ceramics and pharmaceuticals, allowing reliable phase assignment for the complex, multi-component recycled-catalyst materials studied here. Full diffraction results and quantitative phase fractions for the reactivated and modified catalyst series are presented in the companion characterization paper of this series.

## CONCLUSIONS

A complete and reproducible protocol has been established for converting spent titanium dioxide catalyst from the Shurtan Gas-Chemical Complex into ZnPc- and iron-oxide-modified sorbent–photocatalyst materials. The methodology comprises thermal reactivation at 500–650 °C, sequential impregnation with iron oxide and zinc phthalocyanine, and a standardized batch sorption/photodegradation assay using methylene blue as a model pollutant, quantified through a pseudo-first-order Langmuir–Hinshelwood kinetic treatment. This protocol provides the experimental foundation for the detailed physicochemical characterization and photocatalytic performance evaluation reported in the subsequent papers of this series.

## REFERENCES

1. Serpone N. Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis // *Journal of Photochemistry and Photobiology A: Chemistry*. – 1997. – Vol. 104, No. 1. – P. 1–12.
2. Testino A., Bellobono I. R., Buscaglia V. [et al.] Optimizing the photocatalytic properties of hydrothermal TiO<sub>2</sub> by the control of phase composition and particle morphology // *Journal of the American Chemical Society*. – 2007. – Vol. 129, No. 12. – P. 3564–3575.
3. Malato S., Blanco J., Cáceres J., Fernández-Alba A. R., Agüera A., Rodríguez A. Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO<sub>2</sub> using solar energy // *Catalysis Today*. – 2002. – Vol. 76, No. 2–4. – P. 209–220.
4. Oppenländer T. Photochemical Purification of Water and Air: Advanced Oxidation Processes (AOPs) – Principles, Reaction Mechanisms, Reactor Concepts. – New York : Wiley-VCH, 2007. – 368 p.
5. Shan A. Y., Ghazi T. I. M., Rashid S. A. Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: a review // *Applied Catalysis A: General*. – 2010. – Vol. 389, No. 1. – P. 1–8.
6. Fox M. A., Dulay M. T. Heterogeneous photocatalysis // *Chemical Reviews*. – 1993. – Vol. 93, No. 1. – P. 341–357.
7. Su C., Tseng C.-M., Chen L.-F. [et al.] Sol-hydrothermal preparation and photocatalysis of titanium dioxide // *Thin Solid Films*. – 2006. – Vol. 498, No. 1. – P. 259–265.