



Technologies for elimination of chemical hazards

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Hybrid nano-titanium dioxide/diatomite photocatalyst for advanced oxidation processes (AOPs) mediated removal of toxic organic pollutants

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Abstract – Photocatalytic activity of the hybrid photocatalyst (diatomite/titanium dioxide, DTD) based on nano-sized titanium dioxide grafted on the diatomite surface was tested in advanced oxidation processes (AOPs) by measuring degradation of phenol in model contaminated aqueous solutions under UV illumination. The hybrid catalytic system was synthesized via a modified heterogeneous hydrolysis procedure in the presence of diatomite by using titanium tetrachloride as titania precursor. The photocatalyst showed high activity in photocatalytic decomposition of phenol in aqueous solution. The degradation degree was up to 90% in 180 min depending on initial phenol concentration. The experimental results obtained for the photodegradation kinetics of phenol showed a good agreement with the Langmuir-Hinshelwood model of adsorption with the external diffusion as the determining step of the process. The prepared DTD composite at a loading of 2 g/L was able to mineralize phenol under UV irradiation in aqueous solution at initial phenol concentration of 10 g/L within 54 min of photocatalytic process up to the maximum allowable concentration level (MAC) for phenol in wastewater (~5 mg/L).

Keywords: titanium dioxide, diatomite, AOPs, photocatalysis, phenol, mineralization, water treatment.

Технологии ликвидации источников химической опасности

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Гибридный фотокатализатор нано-диоксид титана/диатомит для удаления токсичных органических загрязнителей из воды с помощью эффективных окислительных процессов (AOPs)

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Аннотация – В статье представлены результаты изучения фотокаталитической активности гибридной каталитической системы диатомит/диоксид титана, представляющей собой композит на основе наноразмерного диоксида титана, привитого на поверхность диатомита, которая была применена для разложения фенола в водном растворе под действием УФ излучения, как пример эффективных окислительных процессов типа AOPs (Advanced Oxidation Processes). Катализатор был синтезирован методом модифицированного гетерогенного гидролиза в присутствии диатомита с использованием четыреххлористого титана в качестве прекурсора диоксида титана. Фотокатализатор показал высокую активность в разложении фенола в водном растворе: так, степень деградации фенола достигала 90% в течение 180 мин процесса в зависимости от исходной концентрации загрязняющего вещества. Кинетика процесса фоторазложения хорошо описывается моделью адсорбции Ленгмюра-Хиншельвуда. Полученный композитный катализатор при дозе 2 г/л и исходном содержании фенола 10 г/л удаляет загрязнитель из водного раствора, достигая значений ПДК по фенолу в сточных водах (~5 мг/л) в течение 54 мин фотокатализа.

Ключевые слова: диоксид титана, диатомит, эффективные окислительные процессы, фотокатализ, фенол, минерализация, очистка воды.

INTRODUCTION

In recent decades, the chemical safety of drinking water contaminated by the presence of organic pollutants is increasingly becoming one of the major concerns worldwide. Currently available water treatment technologies, such as adsorption or coagulation are dealing with simple concentrating contaminants present in water by transferring them from one phase to another, but eventually the pollutants still remain intact and are scarcely ‘eliminated’ or ‘destroyed’ completely. Other traditional water treatment procedures such as sedimentation, filtration, chemical and membrane technologies are associated with high operating costs and can lead to the formation of toxic secondary pollutants in the environment.

Alternatively, photochemical technologies are applied which use chemical oxidants in the presence of a suitable catalyst and/or ultraviolet light to oxidize or degrade the pollutants involving a wide range of chemical structures and resulting in their conversion into less toxic substances which are more readily biodegradable. These technologies, known as advanced oxidation processes (AOPs) [1–4], are being extensively explored, particularly, for degradation of various types of pollutants of industrial wastewater [5–7].

AOPs procedures can be especially useful for the treatment of wastewater containing highly toxic organic compounds and pollutants, which can’t be removed using biological procedures, except for water treatment from bacteria, since bacteria are able to be adapted to almost all kinds of toxic environments. AOPs are driven by the formation of highly reactive species, mainly hydroxyl radicals that are capable of breaking down pollutants through oxidation reactions. The AOPs-generated hydroxyl radicals quickly and nonselectively react with organic compounds, which results in complete mineralization of pollutants to carbon dioxide, water and inorganic salts, or at least to the formation of non-hazardous organic compounds [8, 9].

One of the most important types of AOPs is heterogeneous photocatalytic oxidation, commonly known as photocatalysis [10, 11]. With this approach, harmful organic substances are decomposed in the presence of a catalyst and ultraviolet (UV)

irradiation without generating secondary harmful pollutants. The photocatalyst is activated by the absorption of photon and is capable of accelerating chemical reaction without consuming from another energy source.

In general, photocatalysis proceeds in the following five stages:

1. Supply of the reactants from the bulk solution to the catalyst surface;
2. Adsorption of reactants on the surface;
3. Reaction of adsorbed reactants on the catalyst surface;
4. Desorption of reaction products;
5. Removal of the products from the liquid/solid interface.

In aqueous media, the photocatalytic reaction (stage 3) is mostly the photocatalytic degradation of organic pollutants in the presence of a semiconductor as the photocatalyst, more often TiO_2 [12, 13].

At present, AOP-based technology of UV/ TiO_2 photocatalytic oxidation is gradually receiving greater attention in water treatment studies [14–16]. The recent huge research interest in using TiO_2 as a photocatalyst can be attributed to its excellent ability to completely degrade a wide range of organic pollutants to CO_2 plus H_2O due to its low cost, chemical stability and high efficiency properties [17, 18].

Laboratory studies on photocatalysis are typically performed using nano-sized catalyst suspended in the reactor. The catalyst in these experiments is uniformly dispersed in the solution as it passes through the reactor. The uniform catalyst distribution provides very high surface area to volume ratios with lower mass transfer limitations.

However, titania nanoparticles (TNPs) show certain shortcomings in terms of large-scale practical application and commercial profit, which can result in a low photocatalytic efficiency and higher cost: strong tendency to aggregate, difficulties with TNPs recovery from the solution after treatment and low adsorption properties. To overcome these shortcomings, many researchers have been focused recently on immobilizing TNPs on supports having high surface area and excellent adsorption capacity [19–24]. This approach may improve the TNPs distribution in suspension which facilitates adsorption and concentration of target substances.

Recently, porous non-metal minerals have been proposed as supports of TiO_2 -based photocatalysts, such as perlite, zeolite and others due to their low costs.

The support must meet the following requirements: high surface area, sufficient thermal resistance and mechanical stability, inexpensiveness, conformability to reactor configuration, and usability for coating process.

In this context, diatomite can be one of the most suitable supports for titania nanoparticles due to its unique physicochemical properties [25–36]. Diatomite (or diatomaceous earth) is a mineral deposit of diatomaceous algae, which had been accumulated starting from the Miocene period. Amorphous silica is the main ingredient of diatomite, which is usually accompanied by variable quantities of other materials (metal oxides, clays, salts (mainly carbonates), and organic matter). Diatomite is abundant in many locations across the globe and exhibits unique physical characteristics, such as high permeability and porosity (35–65%), small particle size, low thermal conductivity and density along with high surface area [37–39].

Thus, a combination of diatomite and nano-sized titanium dioxide can yield a photocatalyst with high values of specific surface and photocatalytic activity.

Phenols are important chemical compounds in terms of their widespread use in a variety of manufacturing processes. For example, phenol is commonly used in the production of phenolic resins, bisphenol A, caprolactam, and chlorophenols, such as pentachlorophenol. However, these chemicals pose a serious threat to the environment, water supply and human health as a result of their inertness, toxicity, ability to destroy the endocrine system and carcinogenic behavior [40, 41]. The European Union, United States and Canada included several types of phenols on the list of priority pollutants [42–44].

The minimum allowable concentration of phenol in wastewater is 5 mg/L, as prescribed by the World Health Organization (WHO) [45].

Therefore, wastewater contaminated with phenols and similar toxic compounds requires special treatment prior to its discharge into water bodies.

Phenols can be removed from water by means of physical processes, such as flocculation, precipitation, adsorption with activated granular carbon, application of mineral sorbents [46–50] or reverse osmosis [51, 52]. Enzymes and microorganisms have also been used to eliminate phenols [53–56].

However, the application of these processes is limited due to the high cost of the catalyst and the short-term catalytic activity [52]. Biological processes have also been applied to remove phenolic compounds. However, in many cases, phenols inhibit microorganisms to the minimum levels [52, 57].

Advanced oxidative processes (AOPs) have been successful in removing such non-easy degradable contaminants as phenol since they can achieve complete oxidation [58–64].

This work is focused on studying photodegradation of such a toxic substance as phenol from aqueous solution with the help of preliminarily prepared photocatalyst based on nanodimensional TiO_2 deposited on the surface of diatomite (diatomite/titanium dioxide, DTD) under UV illumination. The substantiation of the synthesis method and a detailed characterization of physicochemical and adsorption and structural properties of the obtained composite are described in our previous study [65].

The removal efficiency of phenol from aqueous solution has been studied as a function of catalyst loading, pH of solution, phenol initial concentration using two types of procedures: 1) under dark conditions (adsorption), and 2) under UV illumination (photocatalytic degradation).

EXPERIMENTAL

Samples of the synthesized nanocomposite DTD (~20% TiO_2) were used as adsorbents. DTD was obtained via heterogeneous hydrolysis of TiCl_4 in the presence of a suspension of diatomite. The diatomite used in the study was supplied from the deposits of Vyshkautsy village in the Orgeev region in Moldova after an appropriate purification.

Titanium(IV) chloride (TiCl_4 , 99.9%), ammonia (NH_4OH , 25%) were purchased from Sigma Aldrich.

Typical DTD preparation procedure: 2.0 g of purified diatomite was dispersed in 50 mL of TiCl_4 solution of required concentration to obtain TiO_2 content of about 20 wt.% under continuous of stirring for 30 min; next, drop by drop NH_4OH solution was added until the adjustment of the required pH value and left for stirring within 60 min.

After that, the mixture was centrifuged and the precipitate was separated from the centrifugate, washed with distilled water until the negative reaction for chloride ions was observed, and then dried for 12 h at ambient temperature followed by 4 h at 110°C for 4 h, and further calcined at 450°C for 2 h. The samples were stored in a desiccator at room temperature before their further research and processing. The composition of the starting diatomite and DTD composite are presented in Table 1.

Table 1. Composition of the starting diatomite and DTD catalyst according to atomic absorption analysis data

Sample	Composition, %								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Loss on ignition
D_{in}	79.8	0.11	3.44	0.82	1.46	1.30	0.55	0.35	12.01
DTD	56.0	19.20	2.59	0.53	0.46	0.62	0.25	0.23	10.20
									$\Sigma, \%$
									100.01
									100.14

Material Characterization

Crystal structure, chemical composition and adsorption-structure properties (specific surface area, adsorption pore volume, effective pore radius) of nanocomposite and its components were determined with XRD, XPS and EDX analyses and low temperature adsorption of nitrogen. The specific surface area (S_{sp}), adsorption pore volume (V_s) and effective pore radius (r_{ef}) have been calculated by BET method from nitrogen adsorption - desorption isotherms.

The crystallite size of nano TiO_2 particles (anatase) was estimated by applying the Debye–Scherer equation. The data are shown in Table 2.

Table 2. The adsorption–structural properties of the DTD composite and its components

Sample	% of TiO_2	$S, \text{m}^2/\text{g}$	$V_s, \text{cm}^3/\text{g}$	$V_{\text{ma}}, \text{cm}^3/\text{g}$	$r_{\text{ef}}, \text{\AA}$	$r_{\text{ma}}, \text{\AA}$	$D_{\text{part.}}, \text{nm}$
D_{in}	0	36.449	0.136	1.30	17.40	722	-
DTD	19.2	88.1	0.256	0.879	40.02	200	7.74
TiO_2	100	128.447	0.492	0.276	36.58	43	26.02

Detailed characteristics are presented in the work [65]

Phenol ($\text{C}_6\text{H}_5\text{OH}$, 96%), hydrochloric acid (HCl , 35 wt.%) and sodium hydroxide (NaOH) of analytical grade (for pH adjusting) were purchased from Aldrich (Germany).

For the preparation of solutions, double distilled water was used. All the experiments on the adsorption study were carried out under the following conditions:

Into 50.0 mL of aqueous phenol solution with an appropriate initial concentration 0.1 g of the sorbent sample was added with constant stirring for

equilibration period of time. The amount of adsorbed phenol, a , mg/g was determined using the equation:

$$a_e = \frac{(C_0 - C_e) \cdot v}{m},$$

where C_0 and C_e , mg/L – initial and equilibrium phenol concentration in solution, respectively; v , L – the solution volume; m , g – the sorbent weight.

After adsorption, the solid phase was separated from liquid by centrifugation. Analysis of all solutions for phenol content was carried out spectrophotometrically with diazotized *para*-nitro aniline method according to the known procedure of determination of optical density at the characteristic wavelength of 540 nm using two-beam spectrophotometer KFK-2 (PA ZOMZ, Russia) [66], pH of water solutions were measured using an ionometer I160-M (LLC Antech, Belarus).

All the experiments were conducted in duplicate to verify the results reproducibility.

RESULTS AND DISCUSSION

Determination of optimal parameters of phenol adsorption by DTD

Since the adsorption of a target compound plays a great role in photocatalytic degradation process, a series of experiments was firstly conducted in order to investigate adsorption of phenol elimination on DTD. The adsorption of phenol was studied depending on its initial concentration, pH of the suspension; sorbent dose, and process duration (adsorption kinetics). From experiments carried out in the dark, in the presence of DTD (data are not shown), the optimal parameters for adsorption of phenol by DTD were determined as follows: pH of solution 4.5; sorbent dose 2 g/L; the optimum adsorption time at equilibrium – 180 min.

These parameters were taken as the basis for further phenol photodegradation study.

Photodegradation of phenol using DTD photocatalyst under UV irradiation

The parameters of phenol photodegradation under the action of UV irradiation with DTD as a photocatalyst were studied as a function of the initial phenol concentration, pH of the solution, dose of photocatalyst, and duration of exposure to UV irradiation.

Effect of initial phenol content

The effect of the initial phenol concentration (C_0) on the photocatalytic degradation of the pollutant was studied within the concentration range of 4–18 mg/L at a catalyst loading of 2 g/L. All the experiments were conducted for an irradiation time of 180 min at ambient temperature at pH = 4.5.

The concentration range was chosen due to practical considerations (such concentrations are usually detected in environmental and waste waters).

It was found that the efficient phenol degradation could be achieved over the whole investigated range (Fig. 1).

As expected, the following effect of the initial pollutant concentration on the degree of photodestruction of the phenol was observed: the higher the initial

concentration, the lower the degree of phenol removal from the solution (Fig. 1). Precisely, after 10 min of UV irradiation an elimination yield of 47.9% was obtained for the initial phenol concentration of 4.96 mg/l compared to 16.9% for the concentration of 10.74 mg/L and only 8.7% for the initial phenol concentration of 16.8 mg/L. This can be explained by the fact that with the increase in initial pollutant concentration the number of available sites on DTD surface is reduced due to the adsorption on the catalyst surface which leads to a slowing down in the light penetration affecting the hydroxyl radical generation and pollutant oxidation. Consequently, this results in a decrease in the pollutant removal [67].

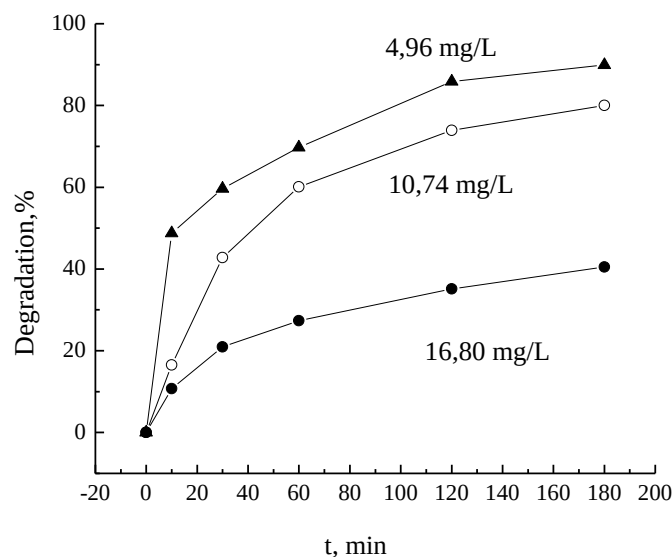


Fig. 1. Effect of initial concentration of phenol on degree of its photocatalytic destruction by applying DTD under UV irradiation (pH = 4.05; T = 20°C, catalyst dose = 2 g/L).

Effect of pH of solution on phenol photodegradation on DTD

The effect of pH on phenol photodegradation degree was studied in the pH range of 3.0–10.0 at phenol initial concentration of 10 mg/L. As can be seen from Fig. 2 (where the whole studied pH range is not shown), the pH of the solution greater than 4.2 does not significantly affect the degree of phenol elimination.

The pH value of 4.5 was further applied to all the subsequent experiments on photodegradation of phenol with photocatalyst DTD to avoid the pH adjustment step.

Photocatalyst dosage is another important parameter which can affect the pollutant degradation. Therefore, it was necessary to study its effect to optimize the photodegradation reaction and to avoid overuse of the catalyst. The experiments were carried out varying the loading of DTD from 0.5 to 4.0 g/L using the following conditions: pH = 4.5, initial phenol concentration of 10.74 mg /L, and irradiation time of 180 min. It can be seen from the data presented in Table 3 that the catalyst dosage plays a specific role in the process studied: photocatalytic degradation of the target compound is gradually increased with the increase of photocatalyst loading up to 2.0 g/L. Further increase in catalyst loading results in decrease of phenol elimination degree.

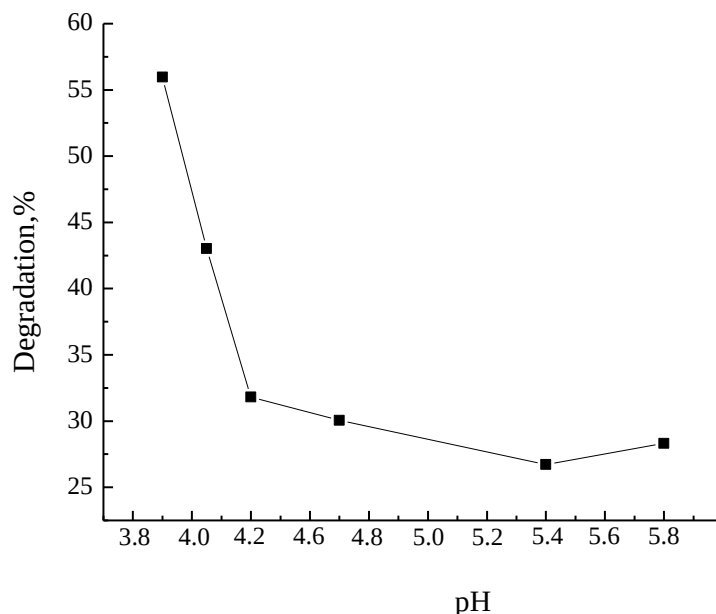


Fig. 2. Dependence of degree of photodestruction of phenol using DTD under UV irradiation on pH of solution (initial phenol concentration 10 mg/L; catalyst loading 2 g/L; T = 20°C, t = 180 min).

Effect of catalyst loading

Table 3. Effect of DTD photocatalyst loading on phenol degradation degree

Catalyst dose, g/L	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Phenol removal, %	8.38	29.32	38.64	55.95	53.44	39.48	25.74	16.76

Thus, 55.95% of pollutant are removed at the catalyst concentration of 2.0 g/L, but only 8.38% of elimination efficiency is achieved for catalyst concentration of 0.5 g/L, and 38.64% for dose of 1.5g/L. The increase in the degradation degree with the catalyst loading was reported to be associated with an increase in the active surface sites of photocatalyst [68, 69].

We assume that the observed phenomenon is apparently due to the initial increase in the number of available photocatalytic sites with the increase of the catalyst dosage. Further on, the turbidity factor starts to be relevant, and the higher the DTD mass, the photocatalytic centers become less accessible for the photon absorption leading to a reduction of $\text{OH}^\bullet$ radicals available for the photocatalytic reaction. A similar kind of effect was reported by other researchers studying photocatalytic degradation of organic compounds [68, 69].

To this end, an optimum photocatalyst concentration of 2 g/L and was applied for the rest of experiments.

Kinetic study of phenol photocatalytic degradation

Duration of the process for phenol degradation using the DTD catalyst under UV irradiation was studied to obtain the equilibration time value.

Fig. 4 shows the dependence of the degree of phenol decomposition on the UV irradiation time. It can be seen, the duration of 180 min is enough to reach the equilibrium. Further increase of time is not accompanied by visible changes in the degree of phenol removal and is found to be unreasonable.

The mechanism of phenol photodegradation on the DTD hybrid nanocomposite under UV irradiation was considered using the Langmuir-Hinshelwood model.

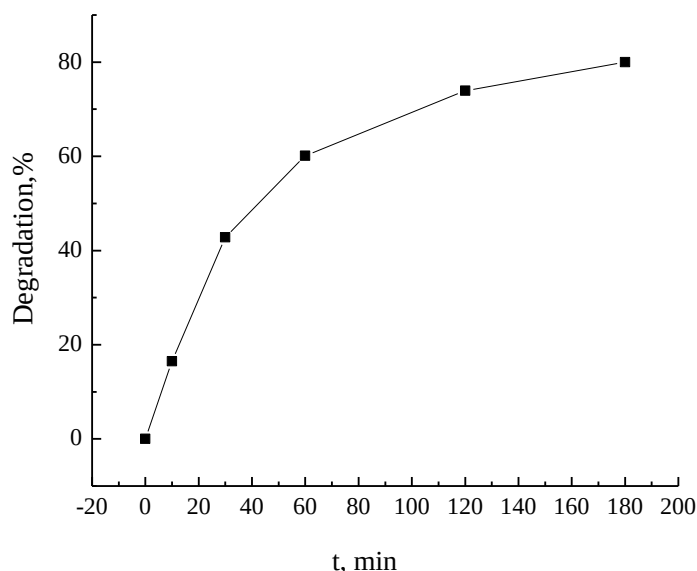


Fig. 3. Kinetics of phenol degradation on DTD photocatalyst under UV irradiation in aqueous solution (pH = 4.5; T = 20°C; catalyst loading 2g /L; C_{in} = 10 mg/L).

For many organic compounds, the effect of their concentration in water on the photocatalytic decomposition reaction rate is often found to fit the Langmuir-Hinshelwood (LH) kinetic model [70, 71].

The L-H model is described by the following equation:

$$C_e = C_o * \exp(-K_{LH} * t + A),$$

where C_e , mg/L, is phenol concentration at equilibrium; C_o , mg/L, is the initial concentration of phenol; K_{LH} is Langmuir-Hinshelwood's constant; t , min, is reaction time; A is the coefficient of the equation.

Fig. 4 represents the results of the corresponding nonlinear modeling using OriginPro 2015 soft.

As can be seen from Fig. 4, the kinetics of phenol photodegradation is well described by the Langmuir-Hinshelwood model (with a correlation coefficient $R^2 = 0.9191$) showing that the reaction belongs to the first order. However, it is difficult to draw a conclusion about the limiting stage from the available results, whether the kinetic area or the diffusion of the agents to the surface limits the reaction; some additional research is needed.

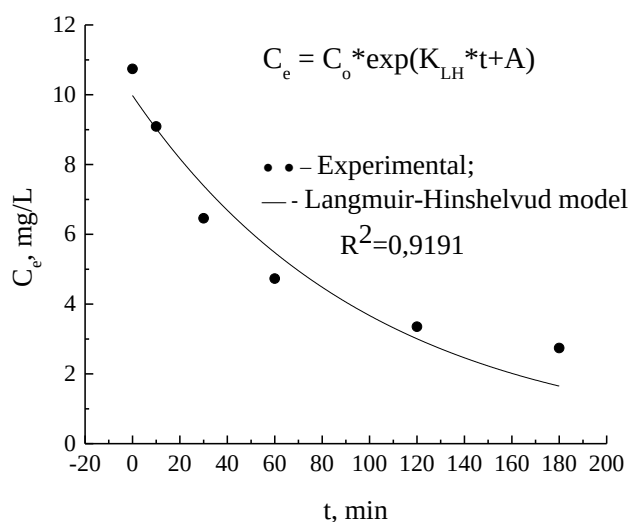


Fig. 4. Kinetics of phenol photodegradation using DTD nanocomposite; experimental data and data obtained by nonlinear modeling according to Langmuir-Hinshelwood model ($C_{in} = 10.74$, pH = 4.5; $t = 120$ min; $T = 20^\circ\text{C}$, sorbent dosage 2 g/L).

Efficiency of DTD in removing phenol to maximum allowable concentration (MAC) level

A series of experiments was performed to investigate the efficiency of photolytic removal of phenol by UV irradiation. The results (Fig. 5) show rather low phenol removal efficiency (6%) under UV irradiation in the absence of a catalyst (i.e. by photolysis).

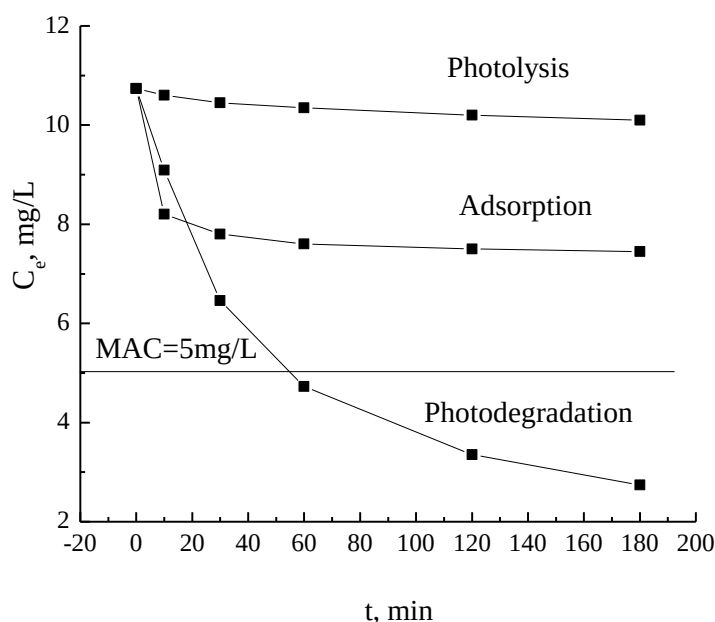


Fig. 5. Comparison of efficiencies of photolysis, adsorption and DTD-photodegradation by time dependences of residual phenol content ($C_{in} = 10.74$ mg/L; pH = 4.5; $T = 20^\circ\text{C}$, catalyst loading 2 g/L).

The results for photolytic phenol destruction were compared with those obtained for adsorption on DTD in dark and photocatalytic degradation in presence of photocatalyst DTD under UV irradiation, and a significant decrease in degradation degree was revealed for photocatalytic data under the same experimental conditions. These results clearly indicate that the phenol degradation observed in the presence of the catalyst is only due to the activity of the catalyst. At the initial phenol concentration of 10.74 mg/L, MAC would have been reached by photocatalytic degradation in 54 min, while during the same time only ~30% of the contaminant was removed by simple adsorption, not to mention that phenol is decomposed during photocatalysis, and upon adsorption, it simply passes into another phase without any change.

CONCLUSIONS

The photocatalytic activity of a hybrid catalyst based on diatomite and nanosized titanium dioxide grafted on its surface (DTD), was studied as an example of AOPs application to phenol photodegradation.

The high efficiency of the DTD photocatalyst was observed in the decomposition of phenol in aqueous solution under UV irradiation: the degree of removal of the pollutant reached 90% in 180 min of photocatalysis.

Adsorption in the dark and photolysis under the action of UV radiation without the presence of a catalyst led to a slight removal of phenol from the aqueous solution.

The photocatalytic removal of phenol was found to be strongly affected by the initial pollutant concentration, pH and catalyst loading. It was shown that photocatalysis with DTD under UV radiation made it possible to achieve the degree of purification of the resulting aqueous solution of phenol, corresponding to the MAC level for wastewater (5 mg/L) at an initial phenol concentration of 10 mg/L, catalyst dose of 2 g/L, and pH = 4.5 within 50 min of the process.

The kinetics of photodecomposition of phenol in the presence of DTD is well described by the Langmuir-Hinshelwood model.

Overall, the presented results indicate that the hybrid photocatalyst derived from diatomite and nanosized TiO₂ can be very effective in AOPs mediated purification of contaminated aqueous solutions from toxic organic pollutants such as phenol.

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