

Application of TiO₂-zeolite as photocatalyst for photodegradation of some organic pollutants

Hossein Faghihian*, Azadeh Bahranifard

Department of chemistry, Islamic Azad University, Shahreza Branch, Shahreza, Iran

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ABSTRACT

Immobilization of catalysts on the surface of some inert supports makes therecovering step easier. Because of the specific physicochemical properties, zeolites are good candidate as catalyst supports. In this study, zeolite X was synthesized by natural kaolin and TiO₂ was incorporated into zeolite phase by impregnation method. Degradation of Safranin Orange, methylene blue and 2,4-dinitroaniline was studied in the presence and absence of ultraviolet radiation. The effect of experimental parameters including TiO₂ loading, photocatalyst amount, irradiation time, pH and initial concentration were studied. Adsorption and photodegradation of the pollutants followed first-order kinetics. Adsorption isotherms were analysed using Langmuir and Freundlich models. The higher activity obtained for TiO₂ supported on zeolite X is attributed to the greater adsorption of the pollutants on the zeolite surface as compared to pure TiO₂.

Keywords: TiO₂-zeolite X; Photodegradation; Adsorption, Safranin Orange, Methylene blue and 2,4-dinitroaniline

1. Introduction

In many industries such as paper manufacturing, petroleum refining, textile processing dyeing of cloth, food and printing many organic pollutants are produced. Since most of these compounds are toxic and cause allergic dermatitis, skin irritation, cancer and mutation in man, their disposal to the environment is one of the major environment control problem [1-4]. Physical adsorption of discharged pollutants by activated carbon is an expensive and commercially unattractive, while adsorption by other adsorbents such as fly ash [5], wood chips [6], natural clays [7] and zeolite [8] is investigated as low cost alternative to activated carbon [9]. A new class of techniques devoted to pollutant remediation is referred as advanced oxidation processes (AOPs) [10-14]. Pollutants could be degraded into harmless matter by AOPs methods under normal temperature and air pressure. Titanium dioxide (TiO₂) is one of the most effective photocatalysts because it is biologically and chemically inert. With near-UV band gap energy, it has no toxicity, low price, high activity, large stability in aqueous media and safe to handle [15-17].

Immobilizing of the photocatalyst on the adsorbent surface is to help the filtration step, reduce losses of the materials and is to give better results in removing organic pollutants [18-23]. Many researchers have examined some methods for fixing TiO₂ on supporting materials including glass beads [24], fibre glass [25], silica [26], and zeolite [27-28]. Among the various supports, zeolites seem to be the most suitable materials due to their unique uniform pores and straight channels. They provide large surface area and most of degradable molecules easily diffuse to the channels and

cages of the order of 4–14 Å resulting in the enhanced degradation [29, 31]. Zeolite X with low Si/Al ratio in the framework possesses high ion exchange capacity, sorption and relatively large pore size that exhibits the highest photoactivity and makes it ideal adsorbent among the various zeolites [32]. In this study, zeolite X was synthesized by natural kaolin which is a raw mineral of low cost and contained of combined source of silica and alumina [33]. TiO₂ was encapsulated in the H-type zeolite by the impregnation of aqueous solution of ammonium titanyl oxalate monohydrate. Safranin-O (SO), methylene blue (MB), 2,4-dinitroaniline (DNA) were chosen as model compounds of photodegradable organic materials. Safranin-O is a biological stain used in histology and cytology that is believed to be carcinogenic in nature, any presence of this pollutant in wastewater would have detrimental effects on marine life. Methylene blue has many uses in biology and chemistry. 2,4-dinitroaniline is used in synthetic intermediate, corrosion inhibitor. It is poisonous and toxic if swallowed, inhaled or absorbed through the skin.

2. Experimental

2.1. Synthesis of zeolite by kaolin

Kaolin from Gonabad region in (North-East of Iran) was taken as Si-Al source for synthesis of zeolite X. It contains some quartz as impurity, which was separated by sedimentation in water. Kaolin was converted to metakaolin by heating in an electrical furnace at

* Corresponding author: Tel.: +98-3213213095;

Fax: +98-3116503191

E-mail: faghihian@iaush.ac.ir

900 °C for 1 h. 4.0 g of metakaolin was added to 20 mL of dionized water and the mixture was homogenized by magnetic stirrer (solution A). 15 mL of 7.8 N sodium hydroxide (NaOH) solutions was added to solution A containing metkaoline. The mixture was shaken until dissolution of kaolin (solution B). In another beaker 2.7g of sodium silicate (Na₂O 8%, SiO₂ 27%, and H₂O 65%, Merck) was dissolved in 10 mL of water (solution C). Solution B was added to solution C and the final mixture was stirred for 1 h. The reaction mixture was aged at room temperature for 48 h and then at 90 °C for 24h under autogenously pressure. Along the synthesis process, the effective parameters such as temperature of crystallization, ageing time were optimized [33].

2.2. Preparation of photocatalyst

To prepare hydrogen form of zeolite X (HX), 100 mL of 1.0N ammonium chloride solution (NH₄Cl) was added to 10 g of sodium form of zeolite (NaX). The mixture was shaken for 24 h at room temperature. The exchanged form was separated and rinsed with distilled water. It was dried at 110 °C for 12 h. and calcined at 400 °C for 4h. Incorporation of TiO₂ into zeolite was performed by introduction of 20 mL of aqueous solution of ammonium titanyl oxalate monohydrate ((NH₄)₂[TiO (C₂O₄)₂]) to 10g of H-X. The mixture was stirred for 12h and the solid phase was filtered, washed with de-ionized water and dried at 110°C. The sample was calcined in air at 200 °C for 5 h [34]. Several preparations were performed, each with known amount of TiO₂ content.

Zeolite and photocatalyst were characterized by X-ray diffractometer (XRD, Bruker, D8-Advance, German with CuK α radiation λ) and FTIR (Nicolet, 400D-Impact, USA). FTIR spectra were obtained in KBr pellets using over the range of 1200–400 cm⁻¹.

2.3. Photodegradation and adsorption studies

To study the dual-effects of adsorption and photodegradation, 20 mL of the pollutant solutions was mixed with 0.02 g of the photocatalyst. The pH of solution was adjusted by HCl or NaOH solution. The suspensions were magnetically stirred at room temperature for known period of time in dark condition and then illuminated by a 30W mercury lamp for photodegradation. The mixture was centrifuged before measurements. The effects of different parameters, such as TiO₂ loading, irradiation time, pH, initial concentration and photocatalyst amount were studied. To optimize each parameter, one of the parameters was varied while keeping other constant. To eliminate the interferences a blank solution was used under identical conditions. The concentration of the pollutants was determined using a UV/Vis spectrophotometer (Cary 100, Australia) at λ_{max} = 519 nm, 663 nm and 250 nm respectively for SO, MB and DNA. The degradation percentage and the amount of adsorption were calculated respectively by the Eqs. (1) and (2):

$$\% \text{degradation} = (C_0 - C_t) \times 100 / C_0 \quad (1)$$

$$q_t = (C_0 - C_t)V / (m \times 1000) \quad (2)$$

Where C₀ and C_t are respectively the concentrations (mg L⁻¹) at initial and given time, m is the amount of photocatalyst (g), V is the

volume of the solution (mL), and q_t is the amount of adsorption (adsorption capacity) (mg g⁻¹).

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3. Results and Discussion

3.1. Characterization of zeolite and photocatalyst

The result of chemical analysis of purified kaolin is shown in Table 1. The SiO₂/Al₂O₃ ratio was about 3.

Fig. 1 shows the XRD pattern of zeolite and the photocatalyst. Due to the small quantity of TiO₂ and its location in zeolite cavities, it was observed that the framework structure of zeolite is unaltered during the inclusion of TiO₂[36, 37].

Fig. 2 shows the infrared spectroscopy (FTIR) of zeolite and the photocatalyst. IR spectrum of photocatalyst is similar to that of zeolite, but a new small band is observed converses a range from 945 to 900 cm⁻¹ which is assigned to stretching vibration of Ti–O–Si, Ti–O–Al [38, 39].

Table (1) Chemical analysis of purified kaolin

Components	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	MgO	TiO ₂	K ₂ O	CaO	P ₂ O ₅	LOI ^a
Weight %	47.1	36.1	0.22	0.46	0.32	0.05	0.06	0.61	0.09	9.55

(a)LOA= loss on ignition

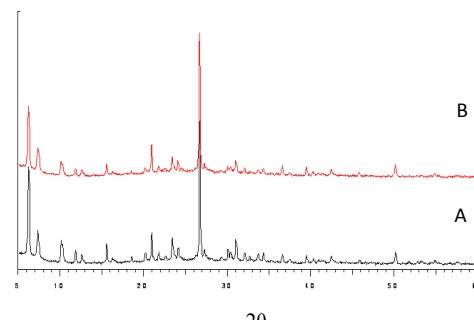


Fig. 1. XRD pattern of zeolite (A) and photocatalyst (B)

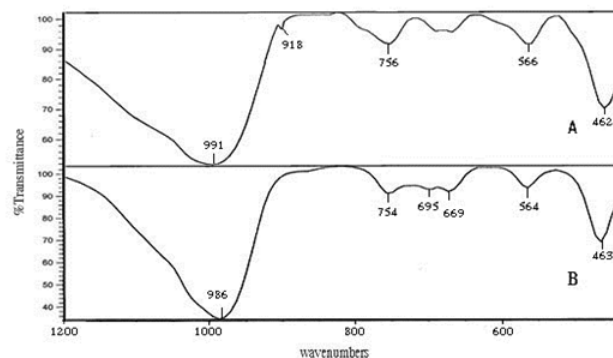
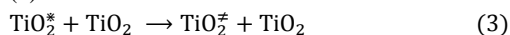


Fig 2 FTIR spectra of photocatalyst (A) and zeolite (B)

3.2. Effect of TiO₂ loading

The samples with different TiO₂ loading were selected to examine the effects of TiO₂ content on the photodegradation and adsorption capacity of the photocatalysts.

As the TiO₂ content of the photocatalyst increases the number of active sites and hydroxyl radicals (OH[•]) increases. This trend continued up to 0.8wt% of TiO₂ for SO, 1.2wt% for MB and DNA. To study the adsorption capacity, the experiments were conducted in dark conditions. It was concluded that the photocatalyst had high affinity towards Mo and the highest adsorption capacity was obtained with photocatalyst contained 0.8-1.2 wt% of TiO₂ (Table 2). However, with higher TiO₂ contents aggregation of TiO₂ on the surface of the zeolite took place with the effect that the TiO₂ particle size increased and its specific surface area decreased [40]. Collisional deactivation would also decrease degradation rate; Eq. (3).



Where TiO₂^{*} and TiO₂[‡] are respectively activated and deactivated species [41].

3.3. Effect of photocatalyst amount

Adsorption and degradation experiments were carried out at different solid/liquid ratios, the results are given in Table 3. Up to 1 g of photocatalyst/L, the degradation percentage increased with increasing photocatalyst amount and then remained constant or decreased. With increasing the photocatalyst amount, the number of available adsorption sites increases which results in increase of the amount of adsorbed pollutants. The decrease in adsorption capacity with increase in the photocatalyst amount is mainly because of adsorption sites which are partially occupied. It also could be attributed to the particle interaction, such as aggregation. Such aggregation and sedimentation would lead to decrease in total surface area of the photocatalyst and an increase in diffusion path length [42, 44].

3.4. Effect of Irradiation time

The effect of Irradiation time on photodegradation of the pollutants is shown in Figure 3. The experiments were carried out by using 20 mL solution of 21 mg L⁻¹(SO), 20mg L⁻¹(MB) and 10 mg L⁻¹(DNA) with 0.02 g of catalyst. The initial rate of the reactions is found to be very fast and thereafter is almost constant. At the beginning, generation of OH[•] is very fast and a large number of vacant surface sites are available for adsorption. After a known period of time, the remaining sites are hardly occupied due to the repulsive forces between the molecules on the surface and in the bulk phase [44]. The formation of intermediates which compete with the parent molecules decreases the reaction rate in the prolonged time. At these conditions, the slow kinetics of degradation after certain time is due to the difficulty in converting the N-atoms of the pollutants into oxidized nitrogen compounds [45,46]. The results indicate that in the presence of photocatalyst and UV irradiation 66% of SO, 83% of MB and 49% of DNA are degraded at the irradiation time of respectively 120,120 and 140 min, while the degradation is much lower in the absence of the photocatalyst.

Table (2) Effect of TiO₂ loading on ([SO] =7 mg L⁻¹[MB] = [DNA] = 10 mg L⁻¹) time length for SO=MB=30 min DNA 120 min, amount of photocatalyst

wt.%) loadin	SO		MB		DNA	
	%degradati	q _t	%degradati	q _t	%degradati	q _t
0.6	60	3	37	5	38	1
0.8	69	4	53	6	42	1
1.2	63	3	55	6	44	1
1.6	61	3	39	4	25	1
1.8	58	3	39	2	20	0

Table (3) Effect of photocatalyst amount ([SO] =7 mg L⁻¹[MB]=[DNA]= 10 mg L⁻¹) time length for SO=MB=30 min DNA 120 min, wt.% of TiO₂ for SO=MB=DNA=1.2)

Photocatalyst g L ⁻¹	SO		MB		DNA	
	%degradati	q _t	%degradati	q _t	%degradati	q _t
0.6	55	5	35	8	17	3
0.8	67	4	41	6	21	2
1.2	69	4	55	6	44	1
1.6	65	3	56	5	24	1
1.8	65	3	56	5	32	1

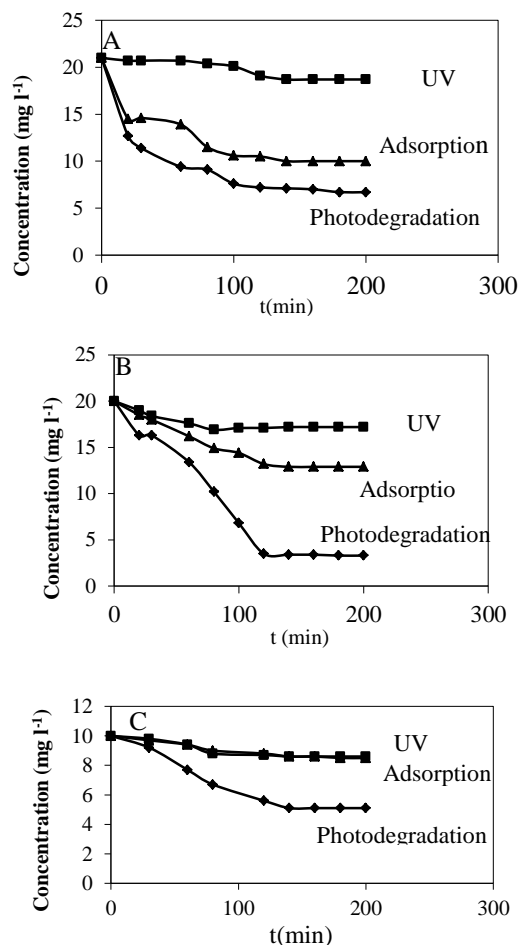


Fig 3 The effect of irradiation time on degradation of safranin-O (A), methylene blue (B) and 2,4-dinitroaniline (C)

3.5. Effect of pH

The effect of pH was studied over the entire pH range of 3–11 for SO, MB and DNA. The influence of pH on degradation depended to the amount of adsorbed pollutants by the photocatalyst and the number of hydroxyl radicals.

The results indicate that increasing the pH of SO and MB solutions leads to increasing degradation and adsorption. The possible reason for this behaviour is that alkaline pH range favours the formation of more OH⁰ due to the presence of large quantity of OH⁻ ions [41].

The degradation of DNA was minimal in acidic and basic solutions. This could be attributed to the protonation and deprotonation of NH₂ group at high and low pH. The optimal pH for SO, MB and DNA was respectively 6.7, 6.7 and 5.8. Table 4.

3.6. Effect of initial concentration

The effect of initial concentration on the degradation of the pollutants is shown in Table 5. The reaction occurs between OH⁰ generated at the active OH⁻ sites and the molecules of the solution. At lower concentration, the number of the available active sites is more than the pollutant molecules, while at higher concentrations, there would be a competition for engaging the active sites. Moreover, with increasing of the pollutants concentration, the light absorption is enhanced with the result that fewer photons reach to the photocatalyst surface [47].

The maximal adsorption was observed at in 21 mg L⁻¹, 30 mg L⁻¹, and 10mg L⁻¹ respectively for SO, MB and DNA.

3.7. Comparison of the photocatalytic activity of TiO₂ and TiO₂-zeolite

The photocatalytic activity of TiO₂ and TiO₂-zeolite on degradation of SO, MB and is shown in Table 6. In the absence of zeolite, the degradation percentage of 19%, 60% and 36% was obtained respectively for SO, MB, and DNA, while with TiO₂-zeolite the values of 88%, 90% and 49% were obtained.

The higher photocatalytic activity of TiO₂-zeolite compared to pure TiO₂ is attributed to the molecules which are adsorbed on the adsorbent sites of zeolite where OH⁰ is available.

4. Isotherm Study

An adsorption isotherm shows how the dye molecules distribute between the liquid and solid phases. The adsorption data fitted to various equations to find a suitable model. In this research, two isotherm models were used. The linear form of the Langmuir and Freundlich equations can be written as shown in Eqs. (4) and (5), respectively.

$$1/q_e = 1/q_{max} + 1/bq_{max}C_e \quad (4)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

Where q_e is the amount of adsorption (mg g⁻¹), C_e is the equilibrium concentration (mg L⁻¹), q_{max}(mg g⁻¹) and b(L mg⁻¹) are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively and K_F [(mg g⁻¹)(L mg⁻¹)^{1/n}], n are the

Table (4) Effect of pH on degradation of the pollutants

SO ^a			MB ^b			DNA ^c		
pH	%degradati	q _t	pH	%degradati	q _t	pH	%degradati	q _t
3	14	2	3	49	4	3	12	0
5.7(Neat dye)	58	2	5.8(Neat dye)	67	3	4.7	19	1
6.7	66	9	6.7	83	7	5.8(Neat dye)	49	1
9.3	67	11	9.2	83	9	6.8	8	1
11	71	13	11	86	9	10.8	6	0

^a [SO] = 21 mg L⁻¹, amount of photocatalyst = 1 g L⁻¹, wt.% of TiO₂ = 0.8, time length =

^b [MB] = 20 mg L⁻¹, amount of photocatalyst = 1 g L⁻¹, wt.% of TiO₂ = 1.2, time length =

^c [DNA] = 10 mg L⁻¹, amount of photocatalyst = 1 g L⁻¹, wt.% of TiO₂ = 1.2, time length =

Table (5) Effect of initial dye concentration on dyes

SO			MB			DNA		
mg L ⁻¹	%degradati	q _t	mg L ⁻¹	%degradati	q _t	mg L ⁻¹	%degradati	q _t
1.7	97	2	5	95	4	5	42	1
7	93	6	10	90	7	10	49	1
14	78	8	20	83	7	15	17	1
21	66	9	30	30	9	20	12	1
28	32	7	40	16	7	30	6	0

^a SO= amount of photocatalyst = 1 g L⁻¹, wt.% of TiO₂ = 0.8, time length = 120 r

^b MB= amount of photocatalyst = 1 g L⁻¹, wt.% of TiO₂ = 1.2, time length = 120 m

^c DNA= amount of photocatalyst = 1 g L⁻¹, wt.% of TiO₂ = 1.2, time length = 140 m

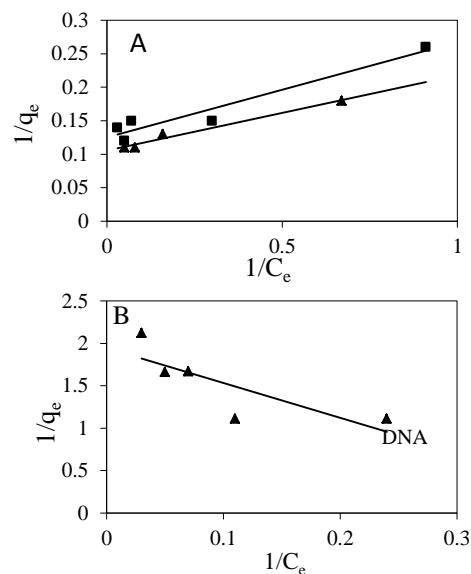


Fig 4. Langmuir adsorption isotherm for safranin-O, methylene blue (A) and 2,4-dinitroaniline (B)

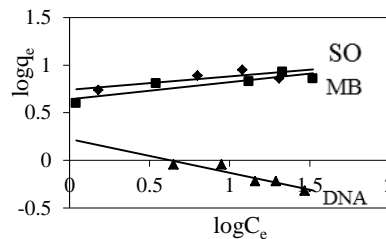


Fig 5. Freundlich adsorption isotherms

Table (6) Comparison of photocatalytic activity of pure TiO₂ and TiO₂/zeolite (pure TiO₂ for SO=5×10⁻³ g L⁻¹, MB = DNA =1×10⁻² g L⁻¹)

Photocatalysts	SO		MB		DNA	
	%degradati	q _t	%degradati	q _t	%degradati	q _t
TiO ₂	19	0	50	1	36	0
TiO ₂ -zeolite	93	7	90	7	49	1

Table (7) Langmuir and Freundlich isotherm parameters

Dye	Langmuir coefficient			Freundlich coefficient		
	q _{max}	B	r ²	n	K _F	r ²
SO	9.52	0.94	0.98	7.19	5.52	0.592
MB	8	0.88	0.931	5.55	4.37	0.876
DNA	0.51	-0.47	0.641	-2.82	1.66	0.865

Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bq_{max}$ and when $\log q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ are obtained [48].

Figs. 4 and 5 were used to calculate the Langmuir and Freundlich constant respectively, and their values are given in Table 7. The Langmuir isotherm model provided the best fit for the equilibrium data for safranin-O and methylene blue in the concentration range investigated, with the maximum adsorption capacity being 9.52 mg g⁻¹ and 8.00 mg g⁻¹, respectively. The adsorption capacity of 2,4-dinitroaniline was negligible and Freundlich model provides better fit to the adsorption data.

5. Kinetic Study

The linearized integrated rate law for first order reaction is given by [49, 50].

$$\ln(C_0/C) = K_{app}t \quad (6)$$

Where C_0 is the initial concentration of the reactant, C is the concentration of the reactant at time t , t is the time length and K_{app} is the apparent constant. When $\ln(C_0/C)$ is plotted against t , a straight line with slope K_{app} is obtained (Fig. 6 and 7). The first order rate constants listed in Table 8. Thus, it is concluded that MB is more prone to oxidative changes compared to the other studied pollutants.

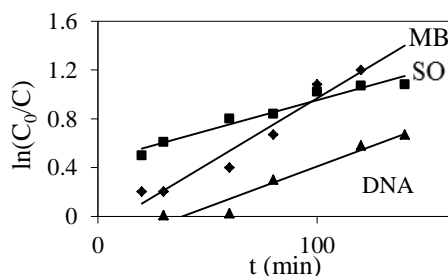


Fig 6. Kinetics of photodegradation of the pollutants.

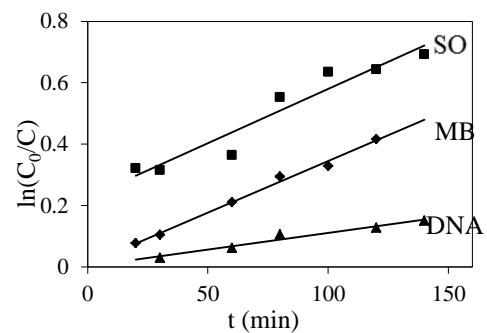


Fig 7. Kinetics of adsorption of pollutants

Table (8) Kinetic parameters for the first order

Dye	Photodegradation		Adsorption	
	k _{app} ×10 ⁻⁵	r ²	k _{app} ×10 ⁻⁵	r ²
SO	5	0.951	3	0.924
MB	13	0.942	3	0.984
DNA	6	0.99	1	0.985

6. Conclusion

Zeolite X has been selected as the host material for the incorporation of TiO₂ due to its three dimensional channels which limits the particle size of TiO₂ during the growth. Combination of the adsorption and photodegradation enhances the removal efficiency of the studied compounds. Adsorption of the pollutants on the photocatalyst surface is one of the key reaction steps in degradation. The removal efficiency of TiO₂-zeolite for the studied pollutants was found to be better than TiO₂ alone. The photocatalyst had both high photocatalytic activity and adsorption affinity towards all the studied pollutants. The adsorption data of safranin-O and methylene blue fitted well to Langmuir equation and that of 2,4-dinitroaniline fitted to Freundlich model. Kinetic data followed the first order kinetic model for all the three compounds.

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