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PREPARATION OF TITANIUM DIOXIDE/ATTAPULGITE COMPOSITES AND THEIR APPLICATION IN TREATING REACTIVE BLACK KN-B WASTEWATER

Removal of water soluble Reactive Black KN-B from aqueous media by means of titanium dioxide/attapulgite (TiO₂/ATP) composites was studied in a batch system. The composites were investigated using X-ray diffraction and surface area analysis. Under UV irradiation, the photocatalytic effect of TiO₂/ATP composites, pH and reaction temperature on the decolorization rate of Reactive Black KN-B were investigated in detail. The adsorption experiments of TiO₂/ATP composites showed that the isotherms and adsorption kinetics were well followed by the Langmuir model and the zero order equation, respectively. The maximum adsorption capacity of TiO₂/ATP composites for Reactive Black KN-B calculated by the Langmuir model was 20.08 mg·g⁻¹. It can be concluded that the TiO₂/ATP composites could be good photocatalysts/adsorbents for treating Reactive Black KN-B wastewater.

1. INTRODUCTION

Degradation of the environment and exhaustion of natural resources reached a stage that is threatening well being of future generation. Therefore, a new and more comprehensive perception of environmental pollution is necessary. Such a revolutionary way of dealing with pollution is provided by the concept of sustainable development [1–4]. It requires slowing exhaustion of resources and restoration of all compartments of the environment. One of the major tasks are to reduce global climate change through low carbon growth [5] and to evaluate carefully the development of contemporary economy [6–9]. Untreated disposal of waste water into the receiving water body damages aquatic life and human beings by mutagenic and carcinogenic effect. In most cases impurities are wasted resources, part of which enters water stream polluting it.

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One of such pollutants are dyes. Their degradation both in chemical or biological processes is widely reported in the literature. Among these methods, adsorption has gained interest in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms [10]. Although activated carbon as an adsorbent has been widely investigated for the adsorption of dyes [11], there still is a need to search for a new, more economical adsorbent due to the fact that the current ones are expensive and difficult to regenerate. One of such adsorbents may be neutral mineral attapulgite (ATP), which is a hydrated magnesium aluminium silicate present in nature as a fibrillar silicate clay mineral. ATP particles, examined under an electronic microscope, create fibrous bundles similar to those of hay. ATP has good colloidal properties, high adsorptive and decolourant capability, and also has a very good plasticity and cohesive force. There are large reserves of ATP in South China, especially in Jiangsu and Anhui Provinces. Therefore, it is expected that ATP-based adsorbents will be satisfactory materials for dye polluted water due to the fact that it has been reported that the modified ATP display higher adsorption capacity than bare ATP [12–14].

In recent years, photocatalytic processes have been treated as alternative methods for water decontamination [15]. Titanium dioxide (TiO_2) is one of the most efficient photocatalysts whose advantages include non-toxicity, chemical stability and high photoactivity [16]. Therefore, natural mineral, a carrier of nanometer TiO_2 photocatalyst, is of great interest because it is cheap and as a natural adsorbent it does not need to be manufactured, and therefore, its use decreases environmental pollution and meets in such a way the sustain ability criteria.

In the present study, TiO_2 /ATP composites were prepared by the sol-gel method and resulting composites were used in the decolorization of a dye, Reactive Black KN-B. The effects of various experimental conditions such as photocatalytic effect of TiO_2 /ATP composites, pH value of reaction system, and reaction temperature were investigated in detail.

2. MATERIALS AND METHODS

Reagents and materials. Attapulgite, with an average particle size of 200 mesh, was supplied by Jiangsu, Maige Sorbent Co., Ltd. Titanium dioxide, Tetrabutyl titanate, Reactive Black KN-B and absolute alcohol were purchased from the Chinese Medicine Group Chemical Reagent Co., Ltd, and all were of analytical grade reagents. Moreover, secondary deionized water was used in all experiments.

Preparation of TiO_2 /ATP composites. The TiO_2 /ATP composites were prepared by the sol-gel method. Typical procedures were the following: firstly, attapulgite powder was ground to less than 100 mesh (screen hole size of 0.15 mm), and matched into 5% water suspension with pH of 11. Then, the solution was stirred for 4 h, age for 24 h at

room temperature with electromagnetic agitator in order to make the attapulgite fiber bundle fully dispersed, which was recovered and reserved after drying. Then the attapulgite powder was impregnated in ethanol solution of tetrabutyl titanate, stirred and mixed evenly. Then, free tetrabutyl titanate which was not adhered to the surface of attapulgite was washed with anhydrous ethanol until there was no white precipitate out in supernatant fluid by monitoring with deionized water, and then ethanol volatilized at room temperature. Finally, attapulgite with tetrabutyl titanate was added into the crucible, which was put into a beaker filled with a small amount of water, then the mixture was heated in the oven up to 60–80 °C with its mouth sealed using adhesive so that tetrabutyl titanate adsorbed at the attapulgite surface was hydrolyzed into titanium hydroxide by water in steam condition. Once hydrolysis reaction was completed, the crucible containing composites was calcined for 3 h in a muffle furnace at various temperatures (400, 500, 600 and 700 °C). then a series of TiO₂/ATP composites were prepared, which were grinded into powder and ready for use [17].

Characterization. X-ray diffraction (XRD) analyses of the powered samples were performed with the use of an X-ray diffractometer with the Cu anode (D/Max 2500 PC, Rigaku Corporation, Japan), running at 60 kV and 30 mA with a scan range from 10° to 70° at 3°/min. The specific surface areas of the calcination samples were measured at 77 K for 1 h by the BET method using a Micromeritics Adsorption Instrument (ASAP2010, Micromeritics, American). The surface areas were calculated from adsorbed nitrogen volume using an automatic volumetric apparatus.

Adsorption/photocatalytic experiments. The experimental methods were selected after a detailed, preliminary investigation. All the adsorption/photocatalytic experiments were carried out by adding 150 mg or 200 mg of TiO₂/ATP composites calcined at 500 °C to 100 cm³ of Reactive Black KN-B aqueous solutions (10 mg·dm⁻³) in a 250 cm³ beaker and then stirred and exposed in UV light of 16 W at the wavelength of 254 nm for a given time. Then, the solution was centrifuged at 3000 rpm for 10 min and the supernatant was filtered using a filter paper. The concentration of filtered fluid was measured using a UV spectrophotometer at the maximum adsorption wavelength of 560 nm. The decolorization rate (D , %) of the dye was calculated by the following formula:

$$D = \left(1 - \frac{A}{A_0} \right) \times 100\% \quad (1)$$

where A_0 and A are absorbances of the solution before and after irradiation, respectively.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF XRD

The XRD patterns of TiO_2/ATP composite are shown in Fig. 1. Only the composite of calcination temperature of 400 °C still reached attapulgite characteristic peaks at 8.34° and 20.10° (Fig. 1a), while the peaks belonging to ATP disappeared completely at higher calcination temperatures.

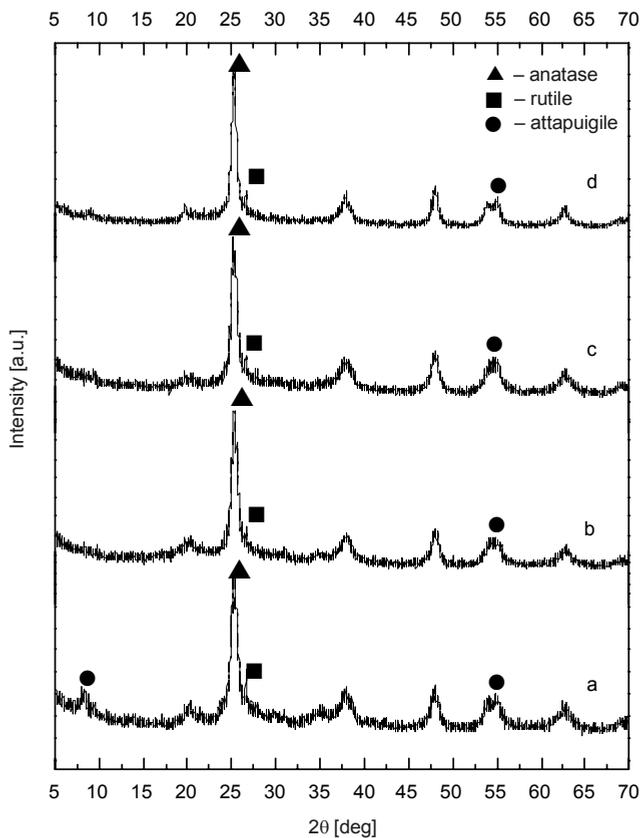


Fig. 1. XRD spectra of TiO_2/ATP composites at various calcination temperatures: a) 400 °C, b) 500 °C, c) 600 °C d) 700 °C

It happened due to the fact that upon increasing calcination temperature the channel of water in attapulgite gradually collapses changing the structure of attapulgite. In Figure 1, those characteristic diffraction peaks can be found at 25.32°, 37.98°, 47.76° and 54.90°, which were consistent with the main peaks of anatase phase TiO_2 ,

where the peak position at 25.32° is typical characteristic diffraction peak of TiO_2 , indicating that there is an obvious anatase type TiO_2 . Also the characteristic diffraction peak of weak rutile type TiO_2 (2θ at 27.54°) appears in the TiO_2/ATP composite prepared by the sol-gel method. This proves that tetrabutyl titanate hydrolyzed and calcined at $400\text{--}700^\circ\text{C}$ formed coexisting anatase type TiO_2 and a small amount of rutile type TiO_2 . What is more, in general, anatase TiO_2 has better light catalytic activity than rutile type TiO_2 . Thus, it can be concluded that amorphous TiO_2 completely coated the surface of ATP during the preparation of TiO_2/ATP composite by the sol-gel method.

3.2. CHARACTERIZATION OF ADSORPTION ISOTHERMS

Table 1 lists the specific surface areas (BET) of TiO_2/ATP composites at various calcination temperatures. Among these, the BET at 400°C was the largest one and others diminished upon increasing temperature up to 700°C .

Table 1

BET of different calcination temperatures of $\text{TiO}_2/\text{attapulgite}$ composites

BET, m^2/g	Calcination temperature [$^\circ\text{C}$]			
	400	500	600	700
	143.4617	117.031	98.5415	75.2241

According to the attapulgite crystal structure and crystal chemical formula, water in attapulgite is present in four states such as surface adsorption water, channel adsorbed water, crystallization water and structure water. The thermal stability of this four kinds of water increases gradually. Along with calcination the temperature increases, the channel of water in attapulgite gradually collapses causing attapulgite structure lose, consequently affecting its specific surface area [18, 19].

3.3. ADSORPTION/PHOTOCATALYTIC EFFECT

The photocatalytic activities of a series of photocatalysts were characterized by the Reactive Black KN-B removal with UV irradiation and natural irradiation. 200 mg of TiO_2/ATP composites were added gradually to 100 cm^3 of dye solutions ($\text{pH} = 6\text{--}7$) to react under vigorous stirring. Then the absorbance was measured every 15 min.

As is shown in Fig. 2, the decolorization rate is higher in the initial stage of the experiment. This indicates that the beginning of adsorption is mainly physical, that is why the adsorption rate is higher. The surface of the composite has a large number of so that a large number of adsorbate particles can be adsorbed at the initial stage of adsorption, the absorption rate is high. Figure 2 also shows that under UV irradiation, the decolorization rate is higher than under natural light, what indicates that TiO_2/ATP

composite is characterized by a very good photocatalytic effect as well as better adsorption performance. This is due to the fact that when TiO_2 semiconductor particles are irradiated with ultraviolet light, electrons (e^-) in the valence band are stimulated to the conduction band and the holes (h^+) in the valence band are produced. Moreover, under the effect of electric field, these holes are separated and migrate to the particle surface, the photo-hole has a strong ability to trap electrons and has a strong oxidation ability. Therefore, in TiO_2/ATP composite also proceeds the decolorization oxidation reaction under UV irradiation.

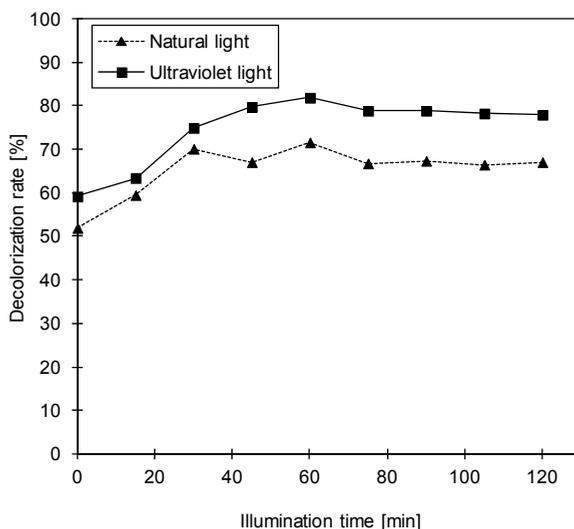


Fig. 2. The decolorization rate of TiO_2/ATP composite on Reactive Black KN-B under various light sources

3.4. EFFECT OF pH

The decolorization effect of the dye on the composites was studied over a wide pH range of 1.0–9.0. 200 mg of TiO_2/ATP composites were added to 100 cm^3 of the dye solution at a given pH. Figure 3 shows that pH significantly affects the extent of adsorption of Reactive Black KN-B. In acidic solution, the lower pH, the better decolorization effect of photocatalytic oxidation is. Furthermore, the decolorization effect in alkaline solutions is also better than in neutral solutions. In acidic solutions, adsorption forces to anionic dye Reactive Black KN-B particles increase upon increasing electropositive attapulgite surface. In alkaline solution, as the zeta potential of Reactive Black dye reduces, the adsorption function of TiO_2/ATP composite is strengthened to anionic dye. Thus, in an overall consideration, all further studies were carried out at pH 3.0.

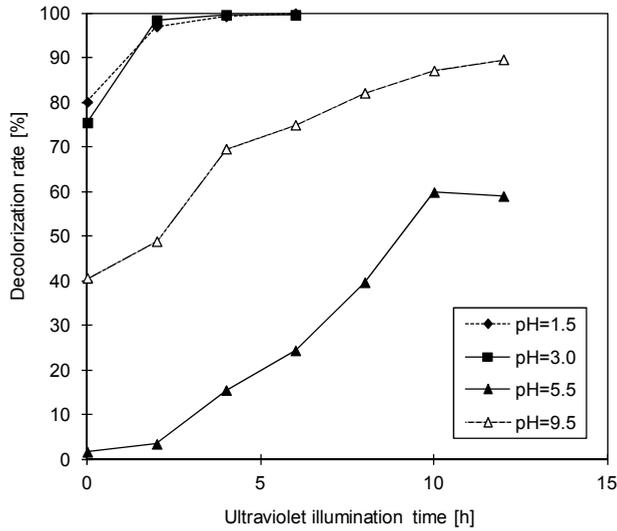


Fig. 3. Effect of pH of the adsorption system on the decolorization rate of Reactive Black KN-B

3.5. EFFECT OF REACTION TEMPERATURE

In order to optimize the design of reaction system to remove the dye, it is important to establish the most appropriate correlation for the equilibrium data for each system.

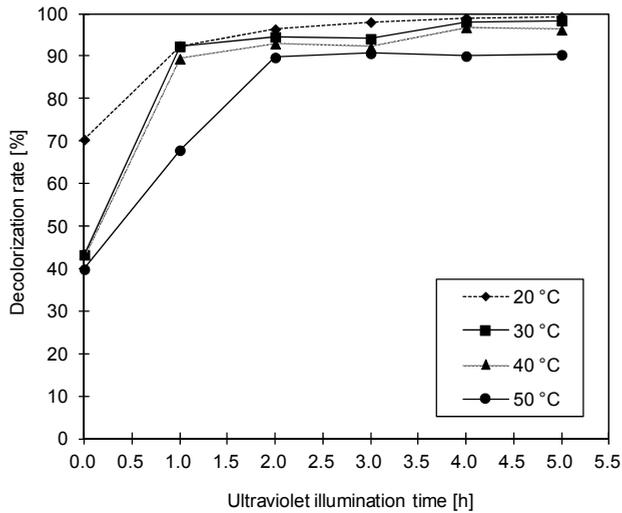


Fig. 4. Effect of temperature of reaction on the decolorization rate of Reactive Black KN-B

When the temperature has a certain value, the relationship between adsorption and equilibrium concentration can be expressed by the adsorption isotherm. The data presented in Fig. 4 were obtained for Reactive Black KN-B adsorption at 20, 30, 40 and 50 °C. As can be observed from the figure, the higher temperature, the lower adsorbed quantity is. Reactive Black KN-B adsorption on TiO₂/ATP composite is an exothermic process, thus, the elevated temperature hinders reaction forward, resulting in saturation in adsorbed particles which declines slightly.

4. ADSORPTION STUDIES

4.1. ADSORPTION ISOTHERM

Adsorbent performance of a catalyst has a certain influence on photocatalytic degradation. In order to examine the effect of adsorption performance of TiO₂/ATP composite to photocatalytic degradation rate, the adsorption of composite calcined at 500 °C to Reactive Black KN-B was investigated. The result is shown in Fig. 5. It may be observed that the composite has stronger adsorption performance to Reactive Black KN-B, the maximum adsorption q_m is up to 19.82 mg·g⁻¹.

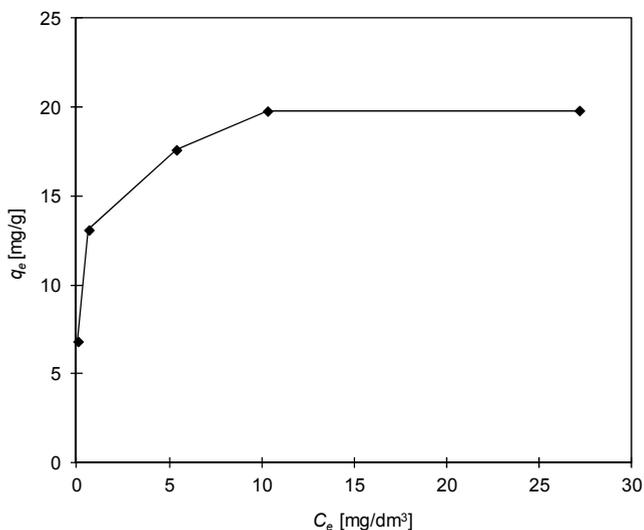


Fig. 5. Adsorption isotherm of Reactive Black KN-B on TiO₂/ATP composite

The adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. The Langmuir model fitted the equilibrium data for Reactive Black KN-B adsorption significantly better than the Freundlich model. According to the Langmuir equation (Eq. (2)), the adsorption equilibrium constant K

can be determined by fitting linear curve to quantify the kinetics of the photocatalytic reaction:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{Kq_m} \quad (2)$$

where C_e is the equilibrium concentration in solution ($\text{mg}\cdot\text{dm}^{-3}$), q_e is the equilibrium adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), q_m is related to the maximum adsorption capacity of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$), K is the adsorption equilibrium constant ($\text{dm}^3\cdot\text{mg}^{-1}$).

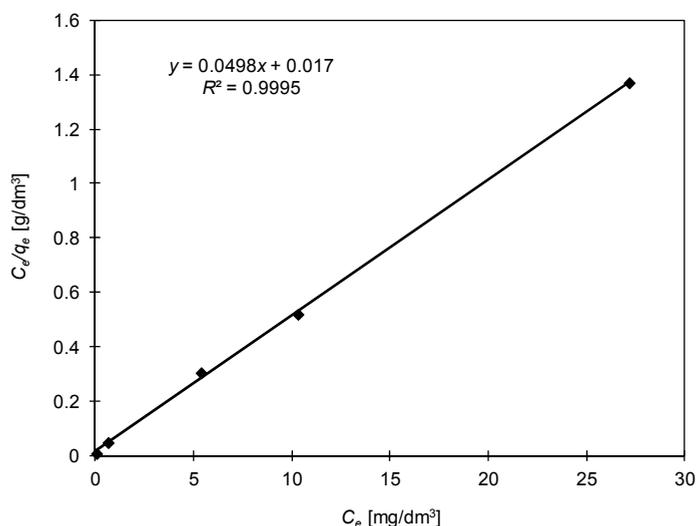


Fig. 6. Langmuir plot for the adsorption of Reactive Black KN-B by TiO_2/ATP composite

As presented in Fig. 6, C_e/q_e has a good linear relationship with C_e . Its fitting equation of the straight line is $C_e/q_e = 0.0498C_e + 0.0170$, the correlation coefficient R^2 is 0.9995 and the maximum adsorption capacity q_m and adsorption equilibrium constant K obtained from calculations are $20.08 \text{ mg}\cdot\text{g}^{-1}$ and $2.929 \text{ dm}^3\cdot\text{mg}^{-1}$, respectively.

4.2. ADSORPTION KINETICS

TiO_2/ATP composite photocatalytic kinetics equation fitted the Langmuir–Hinshelwood model. Using the following first order kinetic equation (Eq. (3)), zero order reaction kinetics equation (Eq. (4)) and between zero order and first order kinetics equation (Eq. (5)), the kinetics of photocatalytic reaction on the composite was analyzed:

$$\ln \frac{C_0}{C_t} = kKt \quad (3)$$

$$C_t = C_0 - kt \quad (4)$$

$$\ln \frac{C_0}{C_T} + K(C_0 - C_t) = kKt \quad (5)$$

where k is the adsorption rate constant, C_0 the initial concentration of a reactant in solution, C_t the reactant concentration in solution.

Table 2

The R^2 values

R^2	First order	Zero order	Between first order and zero order
	0.9396	0.9960	0.9808

The values of the correlation coefficient (R^2) have been calculated from the kinetic equations of various orders and the results are presented in Table 2. It can be seen that zero order kinetics more accurately describes the photocatalytic reaction of the composite than others. The apparent reaction rate k obtained from calculation is 0.1054 h^{-1} , its photocatalytic kinetic equation is $C_t = 0.586 - 0.1054t$.

5. CONCLUSIONS

In this study, TiO_2/ATP composites prepared by the sol-gel method were selected as a cheaper adsorbent/photocatalyst for removal of Reactive Black KN-B from aqueous solutions. It was found that the degradation of Reactive Black KN-B depends on pH and reaction temperature. It was observed that more than 95% of dye removal was achieved by using 150 mg of TiO_2/ATP composite for the initial dye concentration of $10 \text{ mg}\cdot\text{dm}^{-3}$ at pH 3.0. The decolorization rate was highly dependent on pH but changed slightly with temperature as UV illumination time increased.

The adsorption behavior of TiO_2/ATP composite showed that the isotherm and adsorption kinetics were well followed by the Langmuir model and the zero order equation. What is more, the maximum adsorption capacity of TiO_2/ATP composite for Reactive Black KN-B calculated by the Langmuir model was $20.08 \text{ mg}\cdot\text{g}^{-1}$.

The results of this study indicate that TiO_2/ATP composite can be successfully used for the degradation of Reactive Black KN-B from aqueous solutions. Practical application of the composite is however limited due to difficulties in its separation

from the solution after adsorption by centrifugation. Therefore, further research is required in order to explore a new modified method, which could not only separate TiO₂/ATP composite from water effectively but also improve the dye removal rate.

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