Research Article

Preparation of $\text{Na}_2\text{Ti}_3\text{O}_7$ /Titanium Peroxide Composites and Their Adsorption Property on Cationic Dyes

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$\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites (TN-TP) were successfully prepared with the reaction of Ti foils, NaOH, and H_2O_2 at 60°C for 24 h in water bath. The $\text{Na}_2\text{Ti}_3\text{O}_7$ appeared as nanorods in composites. Water bath temperature, water bath time, and the concentration of H_2O_2 and NaOH were crucial. The reaction mechanism was proposed. TN-TP was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and thermogravimetric and differential scanning calorimetry (TG-DSC). TN-TP was a mesoporous material and exhibited stronger adsorption capability for neutral red (NR), malachite green (MG), methylene blue (MB), and crystal violet (CV) than pure $\text{Na}_2\text{Ti}_3\text{O}_7$ and pure titanium peroxide, and the saturated adsorption capacities were 490.21, 386.13, 322.81, and 292.74 mg/g at 25°C, respectively. It was found that the pseudo-second-order kinetic model and the Langmuir model could well describe the adsorption kinetic and isotherm of cationic dyes studied. The results of this work are of great significance for environmental applications of TN-TP as a promising adsorbent material for dyeing water purification.

1. Introduction

Cationic dyes are extensively used in industry, leading to the increasing discharge of dye to the water [1]. The dyeing wastewater reduces the solar light penetration and retards the photosynthetic activity of aquatic plant [2]. In addition, the colored effluence also triggers an increasing toxicity and carcinogenicity, which threatens the water security for human and animals [3]. This resulted in a demand to remove the dyes from effluents. Therefore, the treatment of cationic dyes raised much attention and adsorption has been found to be superior to other techniques for dyeing water purification in terms of initial cost and flexibility [4, 5]. For example, activated carbon has been regarded as an excellent adsorbent and was used widely. However, it was sometimes treated as one-off adsorbent due to the high regeneration cost [6, 7]. It is necessary to search for more efficient and cheaper alternate adsorbents. It had been found that titanate plays important roles of adsorbent in the removal of dyes [8, 9].

In addition, titanium peroxide also causes some concerns in recent researches. Titanium peroxide was first reported as a stable orange solution obtained by the coordination of Ti^{4+} and O_2^{2-} in 1891 [10]. Later, the reaction was applied to measure the concentration of Ti^{4+} and O_2^{2-} [11]. In 1970, the influence of pH on the structure of titanium peroxide was originally studied [12]. In recent years, some studies choose titanium peroxide as a precursor for preparing nanotitanium dioxide [13–15]. It is reported [16–18] that titanium superoxide could catalyze the selective oxidation of aromatic primary amines and phenols. Friese et al. [19] found peroxotitanium complexes can oxidize 2-propanol. Zhao [20] firstly prepared the titanium peroxide power with the reaction of titanium sulfate and H_2O_2 , which showed good selective adsorption property on cationic dyes. There is little research about $\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites at present.

In this work, we successfully prepared $\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites (TN-TP) with the reaction of Ti foils and the mixed solution of NaOH and H_2O_2 (volume

ration 1:1) at 60°C in water bath. The adsorption capabilities for cationic dyes of TN-TP were studied. The adsorption kinetic and isotherm were also studied. It certificated that TN-TP was a promising adsorbent material for dyeing water treatment. So, this work is of great significance.

2. Materials and Methods

2.1. Materials. Cold-rolled titanium foil, 99.5% in purity, was purchased from Baoji Fuxin Nonferrous Metal Products Co., Ltd., China. Hydrochloric acid (37%), sodium hydroxide (NaOH), and nitric acid (67%) were purchased from Beijing Chemical Works. Hydrofluoric acid (40%) was purchased from Tianjin Chemical Reagent Research Institute. Hydrogen peroxide (30%) was obtained from Xilong Chemical Co., Ltd. (China). Methylene blue (MB), neutral red (NR), and crystal violet (CV) were obtained from Tianjin Guangfu Fine Chemical Research Institute (China). Malachite green (MG) was obtained from Tianjin Bodi Chemical Co., Ltd. All reagents were of analytical grade. The water used was distilled.

2.2. Preparation. Ti foils (5 cm × 5 cm × 0.2 mm) were pickled in with a volume ratio of HF:HNO₃:H₂O = 1:3:6 about 30 s at ambient temperature. After ultrasonical cleaning in distilled water, each two pieces of cleaned Ti foils were soaked in the mixed solution (sodium hydroxide solution (10 mol/L), hydrogen peroxide solution (30%), or both of them). Then, the reactants were kept at designated temperature in water bath for a certain time. After cooling to room temperature, precipitates were washed by distilled water for several times until the pH = 7 and dried by water bath at 40°C. The samples were obtained after grinding the dried precipitates. Samples were labeled in Table 1.

2.3. Characterization. XRD patterns were acquired on an X-ray diffraction spectrometer (BRUKER AXS D8 ADVANCE, Cu K α , λ = 1.54056 Å). FT-IR curves were recorded on SHIMADZU 8400s Fourier transform infrared spectrometer. The SEM images were recorded with a model XL 30 ESEM FEG from Micro FEI Philips at room temperature. XPS measurements were carried out with a Thermo ESCALAB 250 spectrometer using an Al K α (1486.6 eV) X-ray source. TG/DSC analyses were performed on a NETZSCH DSC 204 PC Instrument from 30 to 650°C at a heating rate of 10°C/min under N₂ (50 cm³/min at normal temperature and pressure). All of the measurements were carried out at room temperature (25 ± 2°C). The specific surface area was calculated from the N₂ adsorption isotherm using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) mathematical model. The sample was degassed at 50°C for 12 h before test.

2.4. Adsorption Test. All the adsorption experiments were conducted under stirring at room temperature (25°C) in the dark. The general experimental process was described as follows: 0.2 g of the sample was added to 200 mL of dye solution with certain initial concentration. At appropriate time intervals, the aliquots were withdrawn from the suspension

TABLE 1: Samples prepared on different conditions.

Sample	Water bath temperature (°C)	Water bath time (h)	V _{NaOH} : V _{H₂O₂}	State
a	60	24	1:1	Solid
b	70	24	1:1	Solid
c	60	12	1:1	Solid
d	60	24	1:2	Solid
e	60	24	2:1	Solid
f	60	24	Only H ₂ O ₂	Liquid
g	60	24	Only NaOH	Liquid

and the adsorbents were separated from the suspension via centrifugation. SDPTOP UV 2600PC spectrophotometer was adopted to measure the concentration of residual dyes.

3. Results and Discussion

3.1. Preparation of TN-TP. As shown in Figure 1(a), the reaction product of Ti and H₂O₂ (30%) was buff gel with no precipitates after water bath in the study. The yellow gel was proved to be Ti(OH)₂O₂ according to the literature [21]. The reaction product of Ti and NaOH (10 mol/L) was colorless transparent liquid without precipitates as well (Figure 1(b)). This indicated that the insoluble TiO₂ and titanate did not generate in alkaline condition. However, large amounts of light yellow precipitates appeared in the reaction products of Ti, H₂O₂, and NaOH (Figure 1(c)). As a result, the precipitates were the product of the reaction of Ti, H₂O₂, and NaOH. When the pH of the precipitates-containing solution is lower than 7 (hydrochloric acid added), the solution turned to be orange and precipitates in solution began to dissolve (Figure 1(e)); this phenomenon was in accordance with the characteristic of titanium peroxide in low pH solution [12]. After water washing and being dried, the precipitates turned to be yellow (Figure 1(d)), which might be ascribed to the absorbed O₂²⁻ on the surface of precipitates or the O₂²⁻ provided by the titanium peroxide which was one part of the precipitates [20]. As solid titanate was white and solid titanium peroxide was yellow, it could be hypothesized that the precipitate maybe titanate with large amounts of O₂²⁻ absorbed on its surface, a kind of titanate/titanium peroxide composites or pure titanium peroxide.

As titanate was crystallizable, XRD was adopted to identify the reaction product of Ti, H₂O₂, and NaOH after washing, being dried, and grinding. As shown in Figure 2, all of the samples (solid) exhibited a strong peak around 10° and the other three weak broad peaks were around 24.5°, 28.34°, and 48.3°, respectively. Peaks of XRD could be approximately contributed to sodium titanate (Na₂Ti₃O₇ JCPDS number 72-0148) with low crystallinity [22, 23]. In addition, peaks at 10° were concentrated with increasing water bath temperature (sample: (a) → (b)) and the concentration of H₂O₂ (sample: (e) → (a) → (d)), which showed that the interlayered ions crystallinity of Na₂Ti₃O₇ in samples was enhanced [8]. Na₂Ti₃O₇ was generated in each preparation condition, but

FIGURE 1: (a) Reaction product of Ti and H_2O_2 (30%). (b) Reaction product of Ti and NaOH (10 mol/L). (c) Reaction product of Ti, H_2O_2 , and NaOH before washing. (d) Reaction product of Ti, H_2O_2 , and NaOH after washing, being dried, and grinding. (e) Add hydrochloric acid in reaction product of Ti, H_2O_2 , and NaOH (pH < 7).

FIGURE 2: XRD patterns of samples.

crystallinities of them were different, so the reaction product of Ti, H_2O_2 , and NaOH after washing, being dried, and grinding (solid samples) was not the pure titanium peroxide.

As shown in Figure 3, sample (b) prepared at relatively high temperature condition (70°C) and sample (d) prepared at relatively high concentration of H_2O_2 condition consisted of netlike structures with an average diameter of 50 nm and 40 nm, respectively. Titanium peroxide is amorphous in nature [20]; therefore, there was no titanium peroxide in sample (b) and sample (d). The netlike structure was identified to be $\text{Na}_2\text{Ti}_3\text{O}_7$ [24] with low crystallinity according to XRD results. Compared to sample (b), sample (a) which was prepared at relatively low temperature (60°C) consisted of short nanorods and amorphous particles that were adhered on the surface of the short nanorods. Sample (c) was built up by layered sheets (terraces-like morphology) and little amorphous particles in the interlayers of large sheets. Sample (e) was just a large chunk and its surface was smooth. The titanate sheets could split into nanowires by prolonging

the time of Ti foils treated in mixed solution of NaOH and H_2O_2 and then the nanowire layers formed with longer time, finally the netlike structure could be constructed [25]. The morphology change of sample (c) to that of sample (a) was in keeping with the formation of titanate nanowires from the sheets structure. Additionally, high temperature and high concentration of H_2O_2 were conducive to the generation of netlike $\text{Na}_2\text{Ti}_3\text{O}_7$ [26]. So, both XRD and SEM observations presented the coincident results and showed that the short nanorods of sample (a) and the layered sheets of sample (c) were $\text{Na}_2\text{Ti}_3\text{O}_7$.

In order to identify the relationship of amorphous particles and O_2^{2-} , FT-IR was adopted. Figure 4 shows FT-IR spectra of samples. Differences of bands in the region of $400\text{--}4000\text{ cm}^{-1}$ observed were subtle except sample (e), which just had two obvious bands at 1630 cm^{-1} and 453 cm^{-1} . The presence of Ti-OH and hydroxyl groups adsorbed on the surface of samples were confirmed by the appearance of broad intense bands at 3400 cm^{-1} and 3180 cm^{-1} , respectively [9, 27]. There were almost no adsorbed hydroxyl groups on the surface of sample (e). The characteristic peaks around 1630 cm^{-1} and 1385 cm^{-1} could be assigned to H-O-H binding vibration mode and the Ti-O vibrations [9]. The wide band at 453 cm^{-1} in the sample spectra can be assigned to the crystal lattice vibration of TiO_6 octahedra in $\text{Na}_2\text{Ti}_3\text{O}_7$ [9, 28]. It confirmed the existence of $\text{Na}_2\text{Ti}_3\text{O}_7$ in samples, which was consistent with XRD results. The peak at 895 cm^{-1} resulted in the peroxogroups provided by titanium peroxide [20] or excess O_2^{2-} adsorbed on the surface of $\text{Na}_2\text{Ti}_3\text{O}_7$. Peaks of sample (a) and sample (c) at 895 cm^{-1} were obviously stronger than others, which means that they possessed relatively larger amounts of O_2^{2-} . In addition, the peak height at 895 cm^{-1} in descending order was sample (a), sample (c), sample (d), sample (b), and sample (e). Combined with SEM results, the amount of O_2^{2-} was proportional to the amount of amorphous particles in sample (a) and sample (c). As a result, the O_2^{2-} in sample (a) and sample (c) maybe mainly provided by the amorphous

FIGURE 3: SEM images of samples.

FIGURE 4: FT-IR spectra of samples.

particles. As sample (d) is prepared at a relatively high concentration of H_2O_2 , the number of residual O_2^{2-} absorbed on its surface was not the largest. Obviously, the amount of O_2^{2-} absorbed on the surface of samples was limited. The titanium peroxide was the real O_2^{2-} provider. Sample (a) possessed the largest amount of O_2^{2-} . It could be hypothesized that titanium peroxide was present in sample (a).

According to the SEM image of sample (e), the surface of sample (e) was smooth, and few hydroxyl groups and water were adsorbed on it, which could explain why the FR-IR curve of sample (e) had no obvious band at about 3180 cm^{-1} and 1630 cm^{-1} . Combined with the XRD result, sample (e) was considered to be the $\text{Na}_2\text{Ti}_3\text{O}_7$ chunk dropped from the Ti foils.

The XPS was adopted to identify the existing form of O_2^{2-} (absorbed on the surface of $\text{Na}_2\text{Ti}_3\text{O}_7$ or covalently bound to Ti^{4+} to form the titanium peroxide) in sample (a). Before XPS test, sample (a) was dried at 100°C to remove the surface water and surface O_2^{2-} . Figure 5 shows the XPS spectra of sample (a). The peaks at 458.8 eV and 464.4 eV indicated the presence of oxidation state of Ti^{4+} [29]. The O1s spectra showed a main peak at 530.3 eV with two shoulders at 531.7 eV and 533.0 eV . The main peak at 530.3 eV was assigned to the Ti-O in $\text{Na}_2\text{Ti}_3\text{O}_7$. The shoulder peak at 531.7 eV may be attributed to the Ti-OH in titanium peroxide [20]. The peak at 533.0 eV indicated the existence of structural O_2^{2-} in sample (a) [29]. The existence of Ti-OH and structural O_2^{2-} in sample (a) confirmed that sample (a) contains $\text{Na}_2\text{Ti}_3\text{O}_7$ and titanium peroxide. The presence of Na1s spectra at 1071.9 eV indicated the existence of Na-O owing to $\text{Na}_2\text{Ti}_3\text{O}_7$ [30]. The XPS results provided evidence on the existence of titanium peroxide in sample (a).

FIGURE 5: XPS spectra of sample (a).

FIGURE 6: TG-DSC curves of TN-TP.

From the above analysis, sample (a) was proved to be the $\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites (TN-TP). The thermal analysis has been adopted to evaluate the thermal stability of TN-TP to be used as an adsorbent. Figure 6 shows the TG-DSC curves of TN-TP. It could be found that the curve of the DSC exhibited strong endothermic changes from room temperature to 200°C with about 20% weight losses, which should be attributed to residual water evaporation and dehydroxylation on the surface of TN-TP [31]. From

200°C to 400°C, there was no obvious peak in the curve of DSC with just about 4% weight losses due to the release of oxygen which was from the decomposition of peroxide root provided by titanium peroxide [20]. There was no obvious weight loss after 400°C, so water in TN-TP had almost released completely. The $\text{Na}_2\text{Ti}_3\text{O}_7$ was thermally stable from 200°C to 600°C. In the following stage, there was an exothermic peak that appeared at 446.0°C. The titanium peroxide had decomposed to TiO_2 and crystallized with the phase transformation at 446.0°C in this stage. It had been recognized that the temperature was about 450°C at which the transition of anatase to rutile starts [32]. TN-TP possessed good thermal stability from room temperature to 440°C.

The N_2 adsorption-desorption isotherm of TN-TP indicated a specific surface area of 32.26 m^2/g by BET analysis. The corresponding BJH analysis (curve inserted) suggested a predominant pore diameter distribution of 17.4 nm and a total pore volume of 0.233 cm^3/g . The BJH results indicated that TN-TP belonged to mesoporous material.

3.2. Reaction Mechanism. The reaction mechanism of Ti, H_2O_2 , and NaOH was proposed to explain the generating process of $\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites (TN-TP). In alkaline solution, dissociation of H_2O_2 formed the OOH^- ion in reaction (1). Then, the OOH^- ions reacted with Ti to form a metastable and highly soluble peroxide complex $(\text{TiO}_2(\text{OH}))_{n-2}^{4-n}$. Reaction (4) took place immediately in

FIGURE 7: Removal efficiency of samples for MB (initial concentration 400 mg/L, pH = 7, and temperature 25°C).

FIGURE 8: The adsorption curves of NR, MB, MG, and CV at different initial concentration (TN-TP dosage 1.0 g/L).

FIGURE 9: Pseudo-first-order kinetic plots for NR, MB, MG, and CV.

the case of excess OOH^- ions, and reaction (5) followed to generate the $\text{Na}_2\text{Ti}_3\text{O}_7$ [24]. Additionally, with the concentration of Na^+ and OOH^- decreasing, $\text{TiO}_2(\text{OH})_{n-2}^{4-n}$ was going to condense to be stable $\text{Ti}_2\text{O}_5^{2+}$, and then the $\text{Ti}_2\text{O}_5^{2+}$ further formed the titanium peroxide (reaction (6)) [12]. High temperature and high concentration of H_2O_2 were conducive to the generation of $\text{Na}_2\text{Ti}_3\text{O}_7$ but not conducive to the generation of titanium peroxide, so sample (b) and sample (e) were pure $\text{Na}_2\text{Ti}_3\text{O}_7$ without titanium peroxide. By prolonging water bath time, $\text{Na}_2\text{Ti}_3\text{O}_7$ generated with the reaction of excess Ti and NaOH in solution: $\text{Ti} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + \text{H}_2$ [33], which ensured the high concentration of $\text{Na}_2\text{Ti}_3\text{O}_7$ to form the $\text{Na}_2\text{Ti}_3\text{O}_7$ nanorods. Combined with the previous analyses, the best condition to prepare the $\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites (TN-TP) was 60°C -24 h-1:1:

3.3. Adsorption Experiment. The adsorption activities of samples were demonstrated with MB (400 mg/L). As shown in Figure 7, all curves exhibited the same regularity. (1) The concentration of MB decreased dramatically in the first 5 min. This was due to the strong electrostatic interaction between positively charged MB and negatively charged titanium peroxide and $\text{Na}_2\text{Ti}_3\text{O}_7$ with hydroxyl groups absorbed on its

FIGURE 10: Pseudo-second-order kinetic plots for NR, MB, MG, and CV.

surface [20, 34, 35]. (2) Subsequently, the concentration of MB slowed down, and the adsorption rate was slower than that at the beginning stage. It could be explained that the decreasing adsorption points and vacant surface became more difficult to be occupied with reaction advanced, due to the repulsion between adsorbed MB molecules [8].

It was obvious that the curve of sample (a) (TN-TP) decreased fastest in all curves. From SEM analysis, as the titanium peroxide adhered on the surface of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanorods, its molecular structure was not easily damaged and hydroxyl groups firmly bound to the $\text{Ti}_2\text{O}_5^{2+}$ to keep its negativity. In addition, as the titanium peroxide was condensed by the $\text{TiO}_2(\text{OH})_{n-2}^{4-n}$, which can help maintain the hydroxyl groups absorbed on the surface of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanorods, the negative charges of TN-TP can be stable which was constructive to the electrostatic adsorption. As a result, it possessed stronger adsorption ability than pure $\text{Na}_2\text{Ti}_3\text{O}_7$ network structure (sample (c) and sample (e)). As sample (c) was terraces-like morphology, its specific surface area was smaller than that of TN-TP, and so was the adsorption ability.

Four different cationic dyes including MB, MG, CV, and NR were used to study the adsorption property of TN-TP. As can be seen from Figure 8, TN-TP showed great adsorption

effect on them. In addition, the adsorption rates on NR, MG, MB, and CV were different ($\text{NR} > \text{MB} > \text{MG} > \text{CV}$). As the molecular structures were same to each other [20], the smaller the size of the molecular is, the easier the adsorption is. The result also showed that the experimental saturated adsorption capacities for NR, MG, MB, and CV were 490.21, 386.13, 322.81, and 292.74 mg/g at 25°C, respectively. Compared with the pure $\text{Na}_2\text{Ti}_3\text{O}_7$ or pure titanium peroxide, the adsorption capacity of TN-TP increased [9, 20].

In order to investigate the mechanism and characteristics of TN-TP adsorption in dyes removal, the linear plots of pseudo-first-order and pseudo-second-order kinetic models were shown in Figures 9 and 10, and the adsorption kinetic parameters related to models were figured out in Table 2. It can be seen that the trend line of the pseudo-first-order model deviated obviously from the experimental data, but the trend line of the pseudo-second-order model passed through the whole experimental data. Correspondingly, the correlation coefficient values of pseudo-first-order model were lower than those of pseudo-second-order which were higher than 0.9994. The values of $q_{e,\text{cal}}$ estimated from pseudo-second-order model were comparable with the experimentally determined values of $q_{e,\text{exp}}$, which indicated a better applicability

TABLE 2: Equations and parameters of kinetic models and kinetic parameters of dyes onto TN-TP.

Kinetic model		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
Equation		$\ln(q_e - q_t) = \ln q_e - k_1 t$			$t/q_t = (1/q_e)t + 1/(q_e^2 k_2)$			
Capacity term		q_t, q_e : the amounts of dyes adsorbed (mg/g) at time t and at equilibrium, respectively k_1 : the first-order equilibrium rate constant (min^{-1}) k_2 : the second-order equilibrium rate constant ($\text{g}/(\text{mg}\cdot\text{min})$)						
Parameters		$q_{e,\text{exp}}$ (mg/g)	$q_{e,\text{cal}}$ (mg/g)	k_1 (min^{-1})	R_1^2	$q_{e,\text{cal}}$ (mg/g)	k_2 ($\text{g}/(\text{mg}\cdot\text{min})$)	R_2^2
Concentration of NR (mg/L)	50	48.94	236.98	0.0043	0.84331	49.75	0.000074	0.99976
	100	97.65	202.96	0.0403	0.76211	99.01	0.000019	0.99985
	200	193.90	25.15	0.0428	0.73929	194.55	0.000008	0.99997
	400	377.02	16.33	0.0476	0.96544	390.63	0.000002	0.99989
	600	490.21	13.42	0.0163	0.95304	505.05	0.000002	0.99986
Concentration of MB (mg/L)	50	49.18	30.46	0.0480	0.96565	52.36	0.000107	0.99940
	100	97.07	41.92	0.0359	0.89483	100.40	0.000027	0.99985
	200	188.13	112.49	0.0377	0.97510	198.41	0.000005	0.99994
	400	307.02	177.95	0.0329	0.96500	322.58	0.000002	0.99995
	600	322.81	144.65	0.0173	0.92772	331.13	0.000002	0.99997
Concentration of MG (mg/L)	50	49.41	18.29	0.0493	0.87652	50.25	0.000136	0.99997
	100	98.23	34.60	0.0325	0.89785	100.40	0.000028	0.99997
	200	194.89	87.63	0.0361	0.94685	200.80	0.000006	0.99995
	400	359.98	152.06	0.0285	0.92692	370.37	0.000001	0.99996
	600	386.13	150.42	0.0244	0.93031	393.70	0.000001	0.99997
Concentration of CV (mg/L)	50	47.98	11.65	0.0368	0.83537	48.61	0.000172	0.99997
	100	94.84	12.48	0.0316	0.66735	95.33	0.000044	0.99998
	200	177.56	82.06	0.0306	0.92221	183.82	0.000007	0.99989
	400	279.81	142.73	0.0257	0.93305	290.70	0.000002	0.99992
	600	292.74	164.54	0.0186	0.96956	303.95	0.000002	0.99994

FIGURE 11: Langmuir and Freundlich sorption isotherms of NR, MB, MG, and CV on TN-TP.

TABLE 3: Isotherm coefficients according to Freundlich and Langmuir.

Elements	$q_{\max, \exp}$ (mg/g)	Freundlich			Langmuir		
		k_f (mg/g)	$q_e = k_f C_e^{1/n}$ n	R^2	$q_{\max}$ (mg/g)	A (mg/L)	R^2
NR	490.21	0.5349	6.17×10^{-4}	0.90387	497.51	10.45	0.99991
MB	322.81	0.3467	7.20×10^{-6}	0.91099	331.13	6.95	0.99978
MG	386.13	0.3901	1.70×10^{-5}	0.85848	395.26	4.68	0.99993
CV	292.74	0.3807	5.45×10^{-5}	0.90667	304.88	12.37	0.99961

FIGURE 12: FT-IR spectra of the TN-TP and dyes adsorbed on TN-TP.

of pseudo-second-order model to the adsorption of cationic dyes in this study. It also suggested that the rate of the adsorption process was controlled by the chemical adsorption, which involved valence forces through sharing or exchange of electrons between adsorbent and adsorbate [36].

The adsorption process was further studied by two classical isotherm models, Langmuir and Freundlich, as shown in Figure 11. Their corresponding equations and parameters for adsorption of dyes onto the sample are listed in Table 3. It can be seen that the Langmuir model was quite suitable to the adsorption, and the correlation coefficients were higher than 0.9996. In addition, the $q_{\max}$ of NR, MB, MG, and CV calculated through the Langmuir model were 497.51, 331.13, 395.26, and 304.88 mg/g, which was in accordance with the $q_{\max}$ acquired from the experiment.

The FT-IR spectra of the TN-TP and dyes adsorbed on TN-TP were shown in Figure 12. Compared to TN-TP, the additional peaks at 1327, 1193 cm^{-1} (TN-TP-NR), 1392, 1334 cm^{-1} (TN-TP-MB), and 1170, 1367 cm^{-1} (TN-TP-MG, TN-TP-CV) were attributed to the characteristic peaks of NR, MB, MG, and CV, respectively [37–40]. This confirmed the strong electrostatic interaction between the negatively charged TN-TP and positively charged NR, MB, MG, and CV.

4. Conclusion

In summary, the $\text{Na}_2\text{Ti}_3\text{O}_7$ /titanium peroxide composites (TN-TP) were successfully prepared through the reaction

between Ti foils and the mixed solution of NaOH and H_2O_2 (volume ratio 1:1) at 60°C for 24 h in water bath. High water bath temperature (70°C) and high concentration of H_2O_2 (volume ratio 1:2) were conducive to the generation of $\text{Na}_2\text{Ti}_3\text{O}_7$ without titanium peroxide. In the reactions, the $\text{TiO}_2(\text{OH})_{n-2}^{4-n}$ was crucial. TN-TP exhibited stronger adsorption capability for NR, MB, MG, and CV than pure $\text{Na}_2\text{Ti}_3\text{O}_7$ and pure titanium peroxide, and the adsorption capacities were 490.21, 322.81, 386.13, and 292.74 mg/g at 25°C, respectively. It was found that the pseudo-second-order kinetic model and the Langmuir model could well describe the adsorption kinetic and isotherm of the cationic dyes studied. Results of this work are of great significance for environmental applications of TN-TP as a promising adsorbent material used for dyeing water purification.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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