Research Article

Nurdin Bukit*, Eva Marlina Ginting, Erna Frida*, and Bunga Fisikanta Bukit

Physical analysis of TiO₂ and bentonite nanocomposite as adsorbent materials

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Abstract: The research analyzed the physical properties of TiO₂ and bentonite nanocomposite as adsorbent materials. The TiO₂ synthesis method was carried out through a sol-gel process. Meanwhile the synthesis of bentonite was carried out by the ball mill, coprecipitation and addition of cetyltrimethylammonium bromide (CTAB) surfactant. X-ray diffraction nanocomposite characterization showed that the particle size was 17.13 nm. Fourier transform infrared analysis showed the required absorption peak in photocatalysis because the OH group can react with holes and prevent electron-hole pair recombination. The morphology of the nanocomposite showed the occurrence of TiO₂ pillarization in bentonite. The results of the X-ray fluorescence nanocomposite showed that the content of TiO₂ and SiO₂ was 65.22 and 17.4%, respectively.

Keywords: nanocomposite, adsorbent, ball mill, sol-gel, coprecipitation

1 Introduction

Titanium dioxide (TiO₂) is a white pigment material with high brightness and refractive index. TiO₂ accounts for 70% of the total volume of pigment production worldwide and is one among the top five nanoparticles used [1–3].

TiO₂ materials can occur as paints, coatings, inks, pharmaceuticals, food products, cosmetics, and toothpaste. Currently, the production of TiO₂ nanoparticles is quite significant because it has photocatalytic properties. The photocatalyst properties of TiO₂ are functional as solar cells, adsorbent, self-cleaning, anti-fogging, and antibacterial [4–6].

The movement of electrons and holes in semiconductor nanomaterials depends on the effects of quantum confinement, size, and geometry of the material. The specific surface area and surface-volume ratio increase as the material size decreases. The photocatalytic activity of TiO₂ depends on several properties such as crystal phase, surface area, lattice defects, and degree of crystallinity. The use of precursors also affects the quality of TiO₂ nanoparticles. TiCl₄ is a commonly used precursor of TiO₂. It is because TiCl₄ has several advantages such as good thermal stability, being highly reactive and can be used over a wide temperature range, and has a high vapor pressure [7,8]. The mixing of TiO₂ through the synthesis of composite materials improves the properties of TiO₂. In addition, the TiO₂ composite structure can extend the absorption spectrum [9]. The manufacture of nano-TiO₂ with the sol-gel process has been carried out, among others [10,11]. This is because the method works at room temperature [12]. However, the wet phase or sol method is the best way to control particle size, shape, and composition [13].

Bentonite is composed of montmorillonite with colloidal silica produced from the alteration of volcanic glass. Bentonite has calcic variations as a sign that the parent material is basaltic or adhesive. The main content of bentonite is the mineral montmorillonite (80%) with the chemical formula $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4 \cdot nH_2O$. Other contents in bentonite are impurities from several minerals such as quartz, illite, calcite, mica, and chlorite. Montmorillonite structure consists of one layer of alumina (AlO₆) octahedral in the middle flanked by two layers of silica (SiO₄) in a tetrahedral shape [14]. Bentonite has unique catalytic and adsorption properties. Therefore, bentonite is one of the most promising types of material as a safe nanotechnology material [15]. The adsorption ability

* Corresponding author: Nurdin Bukit, Department of Physics, Universitas Negeri Medan, 2022, Medan, Indonesia, e-mail: nurdinbukit5@gmail.com

* Corresponding author: Erna Frida, Department of Physics Universitas Sumatera Utara, 20155 Medan, Indonesia, e-mail: ernafridatarigan@gmail.com

Eva Marlina Ginting: Department of Physics, Universitas Negeri Medan, 2022, Medan, Indonesia

Bunga Fisikanta Bukit: Department of Physics, Universitas Quality Berastagi, 22153, Berastagi, Sumatera Utara, Indonesia

of natural bentonite will be maximized when modifying it. Modification of bentonite has been carried out with various solutions, including HCl, H₂SO₄, and HNO₃ [16–19]. Moreover, pillarization, intercalation of polycations, and calcination also produce a bentonite layer that is stable and constant at high temperatures.

Pillarization of bentonite with TiO₂ can increase the basal distance and specific surface area of the material. It is because TiO₂ has a large specific surface area. So it is possible to be combined with other materials without blocking the pores of these materials. In addition, the effect of GO/TiO₂ nanocomposite in a solution based on natural surfactants on rock samples can be a candidate adsorbent [20,21]. The results of this study are expected to be used as new candidates as adsorbent materials.

2 Materials and methods

2.1 Synthesis of TiO₂ nanoparticles

The TiCl₄ solution was mixed with distilled water and stirred for 2 h using a magnetic stirrer. While stirring, NH₄OH is added to the solution until it turns white. Then, the precipitate was dried at 70°C for 7 h. Figure 1 shows the schematic synthesis of TiO₂ nanoparticles.

2.2 Synthesis of bentonite nanoparticles

The synthesis of bentonite nanoparticles refers to refs. [22,23]. Bentonite was calcined at a temperature of 700°C for 5 h and milled with a ball mill type, planetary ball mill,

for 10 h with a rotation of 250 rpm. Furthermore, the synthesis of bentonite was performed by the coprecipitation method by mixing 6 M HCl using a stirrer at a temperature of 70°C for 4 h. Bentonite was mixed with 7 M NaOH using a stirrer at 70°C for 4 h. CTAB was dissolved in distilled water, heated, and stirred at 80°C for 1 h. CTAB and bentonite were mixed at 70°C for 3 h. The preparation of bentonite nanoparticles is shown in Figure 2.

2.3 Synthesis of TiO₂ and bentonite nanocomposites

Figure 3 shows the preparation of TiO₂ and bentonite composites. TiO₂ and bentonite with a composition ratio (1:1) mixed with deionized water and ethanol were stirred using a magnetic stirrer for 5 h. Then, it was dried in an oven at 100°C for 4 h. Each sample is coded as shown in Table 1.

2.4 Characterization methods

The nanocomposite's phase structure and particle size were investigated by X-ray diffraction (XRD) Goniometer Shimadzu 6000 type using X-ray source Cu/Kα1 at wavelength = 1.54056. The analysis was carried out at an angle of 2θ ranging from 7 to 70°. The diffraction pattern was identified by comparing the diffractogram with the Joint Committee on Powder Diffraction Standard database. Meanwhile, the crystal size (*D*) was determined using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

Figure 1: Schematic of TiO₂ nanoparticle synthesis.

Figure 2: Schematic of bentonite nanoparticle synthesis.

where D is the crystal size ($\text{\AA}$), $\lambda = 1.54056$, θ is the Bragg angle, K is Scherrer's constant with a general value of 0.9, and β is the half-width of the full width at half maximum peak in radians.

The functional group analysis was carried out using a Fourier transform infrared (FTIR) type Shimadzu IR-Prestige-21 made in Japan. The resolution used is 4.0, while the wavenumber ranges from 500 to 4,000 cm^{-1} . The scanning electron microscope (SEM) analysis was carried out using the EVO MA 10 Zeiss instrument, and the chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDS; Bruker Quantax 200). X-ray fluorescence (XRF) characterization was carried out using XRF PANalytical Manipal 4. This tool can be used to test the elemental content of a material ranging from sodium to uranium.

Table 1: Sample code

No	Materials	Sample code
1	Bentonite coprecipitation	Bt
2	Bentonite coprecipitation + CTAB	Bt-CTAB
3	TiO ₂ sol-gel	TiO ₂
4	TiO ₂ + bentonite coprecipitation + CTAB	TiO ₂ -Bt-CTAB

3 Results

3.1 XRD characterization

The XRD pattern in Figure 4 shows a much lower peak broadening and the peak intensity in Bt-CTAB.

Figure 3: Schematic of bentonite and TiO₂ nanocomposites synthesis.

Figure 4: XRD diffraction pattern of (a) Bt, (b) Bt-CTAB, (c) TiO₂, and (d) TiO₂-Bt-CTAB.

Figure 4c shows the rutile phase resulting from the synthesis of the sol-gel method. The broadening and decreasing of the diffraction peaks in Figure 4 are the characteristics of TiO₂, which indicate the successful preparation of TiO₂-Bt-CTAB nanocomposites. Peak reduction is due to the TiO₂ lattice distortion with the addition of bentonite [24,25]. The particle size of the sample is shown in Table 2. Meanwhile, XRD Data Collection shown in Table 3.

The particle size of the TiO₂-Bt-CTAB nanocomposite decreased. The decrease in particle size was also confirmed by the SEM results presented in Figure 6. This decrease shows that bentonite can inhibit the growth of TiO₂ [26–28].

3.2 FTIR analysis

The spectra in Figure 5a and b have the same graph. The absorption band of 1141.47 cm⁻¹ is Si–O–Si. It is confirmed by XRF results, where bentonite has a significant silica content. In addition, a specific absorption peak was found at 3621.59 cm⁻¹, which is the stretching vibration of Al–OH and Si–OH [29].

The absorption bands 2849.43 and 2910.79 shown in Figure 5b are C–H vibrations of the methyl and methylene

groups from CTAB surfactant residues. Figure 5c shows the peak of 747.72 corresponding to the Ti–O vibration in the crystal lattice [30]. Figure 2d shows the absorption bands at 2839.20 and 2,926 cm⁻¹ that are asymmetric and symmetrical strain vibrations of CH₃ and CH₂ of the CTAB aliphatic chain [23]. The absorption band 3621.59 represents the deformation and strain vibration of the OH group, and this band indicates the presence of weak molecules in TiO₂. This property is required in photocatalysis because the OH group can react with holes and prevent the recombination of electron–hole pairs [31,32].

3.3 SEM analysis

The morphology in Figure 6a shows a non-uniform lump of particles. However in Figure 6b, the particles are seen to be distributed, and no streaking occurs. This is due to the interaction between CTAB particles and hydroxyl-Al cations inserted into bentonite, between these ions and the bentonite layer, thus causing the composition of the material, which mainly consists of a layer of bentonite [33].

Figure 6d shows the number of holes on the silicate surface almost entirely in the etched TiO₂-pillared bentonite. This surface implies that the TiO₂-pillared bentonite has many holes etched into the silicate externally and internally. In addition, the agglomeration due to the addition of CTAB forms a block layer [34]. The morphology of the pillared bentonite has a flat layered structure, with a large number of holes between the lamellae, showing good adsorption capacity. The phenomenon of delamination can be ascribed to the fact that TiO₂ as a pillaring agent enters the bentonite interlayers, which can destroy the original structure and enlarge the distance between the layers [35]. In contrast to Figure 6c, which shows a smooth surface consisting of silicates, the surface has not been scratched with chemical reagents on TiO₂ [36]. The number of elements in Table 4 obtained from the EDS analysis is in accordance with that obtained with XRF [37].

3.4 XRF analysis

XRF analysis of Bt and Bt-CTAB in Table 5 shows that SiO₂ and Al₂O₃ are the main constituents of bentonite, with small amounts of other metal oxides [38]. Decreasing the content of SiO₂ and Al₂O₃ with the addition of CTAB is in accordance with the results of previous studies [39].

Table 2: Particle size data

Sample code	Particle size (nm)
Bt	18.47
Bt-CTAB	17.04
TiO ₂	29.60
TiO ₂ -Bt-CTAB	17.13

Figure 6: Morphology of (a) Bt, (b) Bt-CTAB, (c) TiO_2 , and (d) TiO_2 -Bt-CTAB.

Table 3: XRD analysis of Bt, Bt-CTAB, TiO₂, TiO₂-Bt-CTAB

Date	Bt	Bt-CTAB	TiO ₂	TiO ₂ -Bt-CTAB
Crystal system	Trigonal (hexagonal axes)	Trigonal (hexagonal axes)	Tetragonal	Trigonal (hexagonal axes)
Space group	<i>P</i> 31 2 1 (152)	<i>P</i> 32 2 15	<i>P</i> 42/ <i>mnm</i> (136)	<i>P</i> 31 2 1 (152)
Unit cell	<i>a</i> = 4.6764 Å <i>c</i> = 5.2475 Å	<i>a</i> = 4.9160 Å <i>c</i> = 5.4054 Å	<i>a</i> = 4.594 Å <i>c</i> = 2.9589 Å	<i>a</i> = 4.8120 Å <i>c</i> = 5.3270 Å
Density	3.01200 g·cm ⁻³	2.646 g·cm ⁻³	4.248 g·cm ⁻³	2.80200 g·cm ⁻³
2θ angle	26.47	26.48	27.67	27.37
Maximum <i>d</i> _{hkl}	011	110	110	011
Intensity <i>I</i> / <i>I</i> ₀	1,000	1,000	999.	1000.0
Lattice distance <i>d</i> (Å)	3.2061	3.3663	3.2485	3.2823
2θ angle	19.81	30.78	32.74	31.15
Maximum <i>d</i> _{hkl}	100	100	211	100
Intensity <i>I</i> / <i>I</i> ₀	858.2	865.03	480.0	204.6
Lattice distance <i>d</i> (Å)	4.0499	2.9051	1.6876	4.1673
2θ angle	24.19	24.6	36.12	
Maximum <i>d</i> _{hkl}	200	100	101	112
Intensity <i>I</i> / <i>I</i> ₀	527.3	456.40	436.0	107.5
Lattice distance <i>d</i> (Å)	2.0249	3.6537	2.4876	1.7854
2θ angle	34.82	19.68	41.09	54.51
Maximum <i>d</i> _{hkl}	110	011	111	012
Intensity <i>I</i> / <i>I</i> ₀	375.8	371.77	171.0	103.0
Lattice distance <i>d</i> (Å)	2.3382	4.5113	2.1875	2.2443

Meanwhile, the TiO₂ content in the TiO₂ sample synthesized by the sol-gel process was 87.89%, followed by 11.6% Cl. The Cl content probably comes from the TiCl₄ precursor. In TiO₂-Bt-CTAB, the content of TiO₂ and SiO₂ is 65.22 and 17.4%, respectively. The dominant amount of TiO₂ content is probably caused by the distortion of TiO₂ in bentonite.

A discussion of the physical properties obtained and the novelty of this article compared to previous studies are presented in Table 6.

4 Conclusion

Physical analysis of TiO₂ and bentonite nanocomposite shows that these materials can be used as adsorbents. The results of the analysis with XRD show a decrease in the particle size of the nanocomposite. In addition, the FTIR shows deformation and strain vibration of the OH group, and these bands indicate the presence of water molecules that are weakly bound to TiO₂. This characteristic is needed in photocatalysis because the OH group

Figure 5: FTIR of (a) Bt, (b) Bt-CTAB, (c) TiO₂, and (d) TiO₂-Bt-CTAB.**Table 4:** The number of elements detected through EDX analysis

No.	Elements	Bt wt(%)	Bt-CTAB wt(%)	TiO ₂ wt(%)	TiO ₂ -Bt-CTAB wt(%)
1	Ti	0.70	—	34.91	40.82
2	O	51.40	47.33	45.66	30.00
3	Ba	—	—	15.21	25.35
4	F	—	—	—	1.39
5	Si	27.57	23.52	4.21	1.13
6	Al	11.24	14.77	—	0.90
7	Cl	—	—	—	0.39
8	Ag	1.37	4.37	—	—
9	Fe	3.53	3.61	—	—
10	Mg	2.38	2.85	—	—
11	Na	1	2.50	—	—
12	K	0.81	1.07	—	—

Table 5: Elements obtained from XRF analysis

Compound	Bt (%)	Bt-CTAB (%)	TiO ₂ (%)	TiO ₂ -Bt-CTAB (%)
TiO ₂	2.04	1.68	87.89	65.22
SiO ₂	57.3	51.9		17.4
Al ₂ O ₃	17	14		8
K ₂ O	1.18	1.1		0.3
CaO	3.78	3.06	0.15	1.27
V ₂ O ₅	0.05	0.04		0.42
Fe ₂ O ₃	18.9	14.3		5.26
P ₂ O ₅		0.6	0.02	0.3
WO ₃			0.11	0.13
PtO ₂				
Br		13.1		1.6
Cl	—		11.6	
ZnO	0.03	0.052		0.07

Table 6: Discussion of the physical properties obtained and the novelty of this article

Physical properties	Research result	Previous result
Particle size	17.13 nm	15.9 nm [40]
Distance between layers	4.1673 Å	16.9807 Å [36]
Morphology	The number of holes on the silicate surface is almost entirely in the etched TiO ₂ pillared bentonite. This surface implies that the TiO ₂ pillared bentonite has many holes etched into the silicate externally and internally. In addition, the agglomeration due to the addition of CTAB forms a block layer	TiO ₂ particles have been inserted into the bentonite surface of the smaller TiO ₂ grains on the outer surface of the bentonite [41]

can react with holes and prevent the recombination of electron-hole pairs. SEM results describe the pillarization of TiO₂ on bentonite, which was confirmed by XRF.

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