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EFFECT OF DIFFERENT SURFACTANS ON THE FORMATION AND MORPHOLOGY OF TiO_2

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Abstract

TiO_2 is one of the compounds that researchers especially material scientists have studied most recently. Due to some of its extraordinary properties, for example, it can be used in photocatalysis, dye-sensitive solar cells and biomedical devices, are important parameters that make TiO_2 curious. Synthesis, researches and new discoveries made in this direction have always been remarkable. In this study, a low cost and easily prepared surfactant supported hydrothermal method was used to determine the effect of different surfactants on morphology and crystallinity. Three surfactants were selected, including anionic, sodium dodecyl sulfate (SDS), cationic, cetyltrimethylammonium bromide (CTAB) and nonionic (TritonX-100), respectively. Addition of surfactant produced more dispersed and stable TiO_2 in the aqueous suspension. 0.5%, 1%, 1.5%, 2% and 2.5 % by weight of all types were added and 2% surfactant was found to produce the most stable suspension with high turbidity and measurable particle size. CTAB was found to provide a more stable TiO_2 suspension than SDS and triton x attributed to electro-steric.

Key Words: TiO_2, surfactant assisted synthesis, SDS, CTAB, triton-x

1. Introduction

New nano-sized materials and particles are used in very important studies in technology, especially in engineering, due to many improved properties compared to their counterparts. Nanotechnology has the ability to transform the specific properties of most man-made objects and activities by producing nano-sized materials and particles of specific size, shape, and crystal configuration (Mansoori,2005). Titanium dioxide nanoparticles are widely used, as the production and application of nanoparticles produced in commercially available products is increasing very effectively. Nano-TiO_2 has been applied as a pigment in paints, papers, plastics, cosmetics and nanofibers and is used in many fields thanks to its great photo-stability, porosity, ion exchange capacity and characterized superior properties [Hoffman et al.,1995; Wiesner et al.,2006; USEPA,2007). Titanium dioxide or titania (TiO_2) It was first produced commercially in 1923 using various ores (Liu et al.,2012).

TiO_2 has 3 different crystal forms. These; Anatase, Rutile and Brokite crystal structures. Anatase TiO_2 has been used in very wide areas recently, some of them; heterogeneous catalysts, photocatalysts, solar cells, gas sensors and waste water treatment systems. Rutile TiO_2 has the highest refractive index among these three phases compared to anatase and brookite. Therefore, it is generally used in paint raw materials and cosmetics industry. The anatase crystal form shows the highest photocatalytic activity among the other crystal forms. Hence, Anatase TiO_2 constitutes the majority of the studies. However, there are studies that show higher photocatalytic performance than pure Anatase in different ratios of Anatase and Rutile mixture. Commercially used TiO_2 nanoparticles called Degusa P-25 consist of a ratio of 3:1 (Anatase to Rutile). Apart from the effect of different ratios in the crystal structure on photocatalytic activity, changes in the size of TiO_2 particles also have serious effects on photocatalytic performance. Degusa P-25 consists of nanoparticles between about 25-85 nm (Ohno et al.,2001; Kim et al.,2005; Wang et al.,2014; Lu et al., 2016; Zhao et al.,2017; Dokan and Kuru ,2020). Normally, TiO_2 particles are very little toxic and insoluble in water (Hygienists,1986). Therefore, the control material is used as a "negative control" in the artificial environment "in vitro" and "in vivo" toxicological studies (Zhao et al.,2009). However, in addition to these features, in previous studies, it is known that there is progression in lung tumor in experimental mice exposed to these particles at high doses and for at least 2 years (Lee et al.,1985). There are studies on different diseases seen in experiments on different animals (Shi et al.,2013). Although it is known that

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TiO_2 particles do not react chemically (inert), changes in inert properties have begun to be observed with the reduction of the size of the particles and their reduction to nano size. As a result of the decrease in particle size, the surface areas of the particles increase and become more active. In 2006, the International Agency for Research on Cancer-IARC re-evaluated the carcinogenic degree of TiO_2 on the grounds that there is sufficient evidence in animal experiments, although TiO_2 nanoparticles do not have sufficient data in human experiments (Iafro ,2006). As a result of this evaluation, TiO_2 nanoparticles were included in the group of materials with "possible carcinogenic effects in humans". As a matter of fact, findings supporting this decision of IARC have been obtained in studies conducted in recent years. It is not entirely clear in which regions TiO_2 nanoparticles show carcinogenic effects in humans and animals (Lavicoli et al.,2012). In addition, studies are ongoing on the exposure time and size of these particles. For example, in a study by Lin et al., It was observed that the model bacterium Escherichia coli (E. coli) caused damage to the cell walls in direct proportion to the reduction in the size of Anatase TiO_2 nanoparticles varying between 10-50 nm (Lin et al.,2014). As shown in these studies, separating the nano-sized particles from the water as much as possible at the end of the treatment of polluted water is very important for human and environmental health.

When the literature studies are examined, because of all these reasons, TiO_2 synthesis varies according to the place of use. For whatever purpose it will be used, its synthesis should be planned accordingly (Livage et al.,1988; Look and Zukoski ,1992; Look and Zukoski ,1995; Vorkapic and Matsoukas,1998; Zeng et al.,1998 Sugimoto et al.,2003; Sugimoto et al.,2003). In this study, we examined the synthesis of TiO_2 with 3 different surfactants in different concentrations with a new approach. The changes in crystal properties and surface morphologies after treatment with these surfactants were investigated.

2. Materials and Methods

2.1. Synthesis of TiO_2 With Different Surfactants

In the first part of this study, it was aimed to synthesize pure TiO_2. In this study, the Hydrothermal method was applied by evaluating the literature studies because small-sized powders with homogeneous distribution cannot be obtained by sol-gel and other common methods. The temperature vapor pressure chosen for the synthesis we have developed should be preferred to be higher than the boiling point of water to reach a saturated value. The formation of TiO_2 microspheres can only occur with hydrothermally distilled water and titanium agents. Precipitates are formed by adding 0.5 M absolute ethanol C_2H_5OH to a solution of titanium (IV) butoxide ($C_{16}H_{36}O_4Ti$) in distilled water and then peptizing in tetra ammonium hydroxide ($(CH_3)_4N(OH)$) at 80° C for 2 hours. The occurred precipitate filtered and subjected to a temperature of 200°C for 2 hours to obtain a powdery material. The powder washed several times in distilled water and ethyl alcohol, then dried at 80°C. The powder particles were heated at 600ºC for 4 hours to obtain pure TiO_2. In the second part of the study, we tried to obtain TiO_2, which we managed to obtain in pure form, with different surfactants this time and made various analyzes to observe their effects the synthesis process was repeated using a saturated solution to prepare high surface area mesoporous TiO_2 materials with modified hydrothermal (Yuenyongsuwan et al., 2014), respectively. For this, we added surfactants to the environment in the first stage (0.5 M absolute ethanol C_2H_5OH) +titanium (IV) butoxide ($C_{16}H_{36}O_4Ti$) of the synthesis. In Fig. 1, the experimental steps of samples produced by the surfactant supported hydrothermal methods are given.

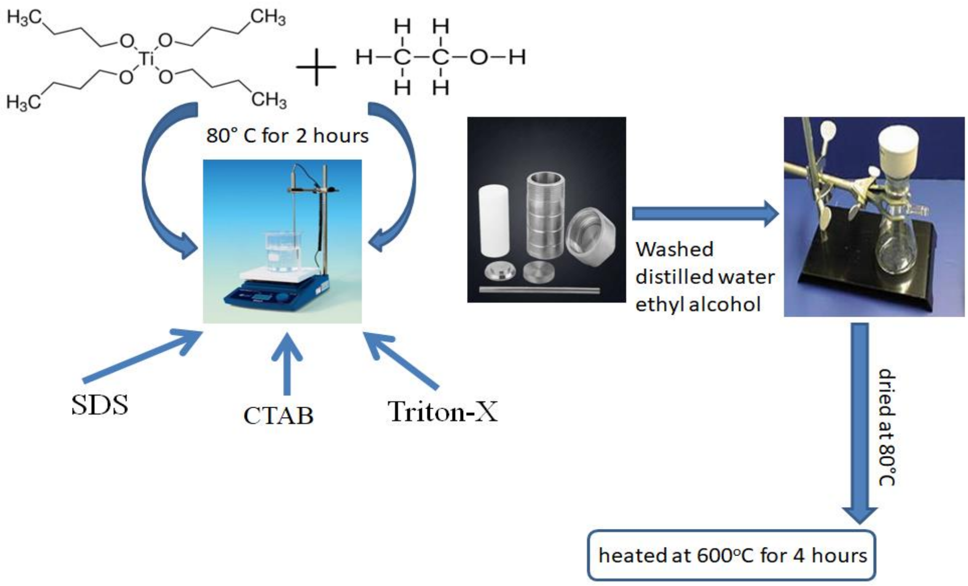

Figure 1. Schematic illustration of TiO_2 synthesis by surfactant assisted hydrothermal method.

3.Results

Stability of samples in aqueous solution was determined by using UV- VIS. For this, T% values relative to time were measured. Crystal properties and phase changes of all samples were examined by X-Ray Diffraction Method (XRD, Pananalytic Imperial). XRD measurements of synthesized samples were made using 0.02° step angle at 40 kV and 40 mA, in the range of 2 ϴ = 10-90°. We also investigated effect of different surfactant on the calculated crystallite size values. We correlate the data with field emission scanning electron microscopy the surface morphology of all samples was investigated by Field Scanning Electron Microscope (FE-SEM, Zeiss) and surface area measurements were characterized by N_2 adsorption / desorption measurements (micromeritic-Gemini IV).

3.1. Surfactant Effect on Phase and Size Controlled TiO_2

The % T was converted into the turbidity value using the equation using Beer Lambert's Law as specified in Equation 1.

$$\text{Turbidity} = 100 - \%\,T \qquad \text{(Eq.1.)}$$

% Transmittance data were recorded 1 hour after the redistribution time. Figure 2 shows the haze trend as a function of surfactant concentration for all surfactants used in the test. In this study, the turbidity value was used to determine the ability of TiO_2 particles to remain dispersed in suspension. High turbidity reflects the distribution of the powders in the suspension, while low turbidity indicates that most particles precipitate to the bottom of the suspension. Among all surfactants, CTAB shows the highest turbidity while triton X is the lowest. In contrast, SDS and triton X show less turbidity in surfactant <1.5% by weight than the control sample. All TiO_2 and surfactant suspensions show that 2% by weight of the surfactant concentration has the highest turbidity, ie about 40-50. The turbidity starts to decrease at 2.5% by weight for CTAB and SDS, but increases slightly for triton X. As a result of the analysis given in the characterization section, it was chosen that the optimum surfactant amount.

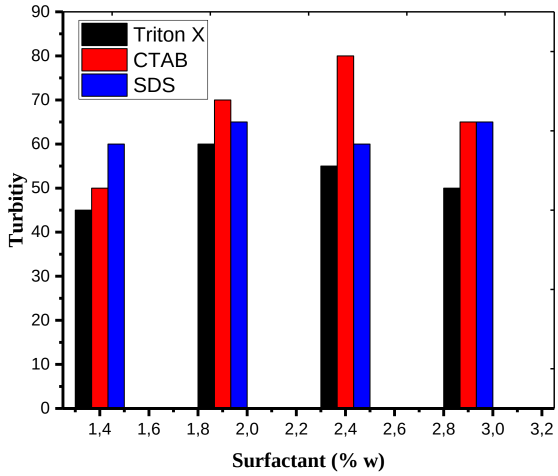

Figure 2. Turbidity of TiO_2 suspensions as a function of surfactant concentration.

3.2.XRD Analysis

The XRD measurements of TiO_2, which we synthesized with different surfactants, are shown in Figure 3. The phase structures of samples were investigated by X-ray diffraction (XRD, Pan analytic Imperial) measurements on a diffractometer operated at 40 kV and 40 mA using CuKα radiation in the 2θ range of 10°–90° with a scan rate of 0.02°. The XRD graph of samples is given in Fig.1. The resulting spectrum belongs to the pure phase, identified by PDF number 01-071-1167. XRD patterns were indexed using Diffrac Plus and Win-Metric programs and unit cell parameters were calculated. As can be seen from the XRD patterns, pure anatase peaks are obtained. Differences in surfactant usage were not observed from XRD spectra. In order to examine the changes made by surfactants in crystal sizes, we calculated the crystal sizes from equation Debye-Scherrer. The crystal size of the synthesized samples was calculated from the XRD pattern using the debye-scherrer equation given in Equation 2 (Yuenyongsuwan et al., 2014).

$$d = \frac{0.94\lambda}{\beta.\cos\theta} \qquad \text{(E.q.2)}$$

Where λ is the wavelength of the x-ray, θ X-ray diffraction angle, and β is the width of the half-peak height in radians. The half-peak height width (FWHM) value, β was calculated from the XRD pattern using the Topas program.From Figure 3 and table 1, they were shown that the diffraction pattern peak intensity of the TiO_2 changes with the type of surfactant. These results suggested that the choice of surfactant is critical in the synthesis of TiO_2. The presence of sodium dodecyl sulfate (SDS) anionic, cetyltrimethylammonium bromide (CTAB) cationic, and nonionic (TritonX-100) in TiO_2 suspensions leads to the change of crystal size. The electrostatic interaction could occur between the OH- groups of TiO_2 with the cetrimonium(hexadecyltrimethylammonium) cations of CTAB. These results are in agreement with previous studies done by HAK Che et al. Suspension containing SDS although show higher Crystal size than CTAB (Rohaida et al., 2018). This is also supported by the larger particle size for TiO_2 added with SDS than CTAB. SDS is an anionic surfactant with sulfate groups as the active site for interactions. (Pandey et al., 2013). The goal of this work is the preparation of mesoporous TiO_2 materials with high specific surface area via optimized hydrothermal process. Thus, this study suggests TiO_2 particles suspension is stabilized better by the repulsive forces from excess cationic attributed from electrostatic interaction between TiO_2 and CTAB and also from steric repulsion of CTAB (Safaei-Naeini et al., 2012) With the addition of Triton x, the crystal size decreased, the most important reason for this may be that crystal growth was prevented by ensuring more homogeneous distribution of the particles during synthesis (Greenwood and Kendall ,1999).

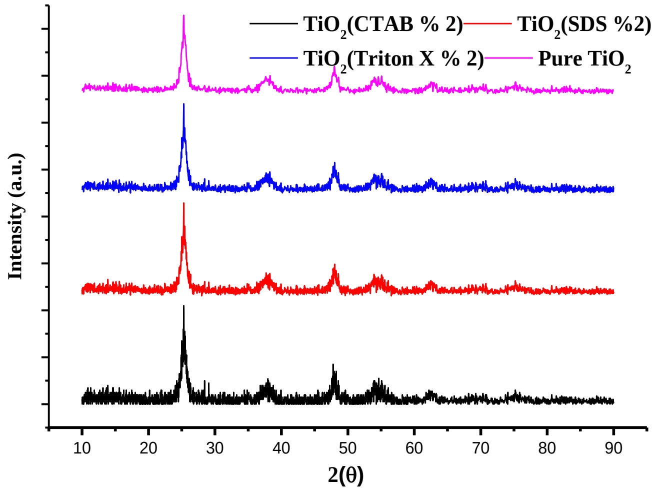

Figure 3. XRD patterns of the TiO_2 materials with different surfactant additives a) sodium dodecyl sulfate (SDS) b) cetyl trimethyl ammonium bromide (CTAB), and c) nonionic (TritonX-100) in TiO_2 suspensions.

Table 1. Crystalline characteristics of samples.

Sample	**Average crystallite size, D (nm)**	**Bet surface area m^2/g_Pore Size(nm)**	**Particle Size (nm)**
TiO_2	130	30_ 63	150-200
TiO_2(CTAB %2,5)	85	66_367	130-170
TiO_2(SDS%2,5)	90	41_183	120-200
TiO_2(TRİTON X%2,5)	95	92_107	130-200

3.3.FESEM Analysis

Particle morphologies of were also assessed through examining their surface morphology the samples were observed by scanning electronic microscopy (FE-SEM, Zeiss), and images are shown in Figure 3 and 4. As can easily be seen in Figure 3 and also table 1, the particle size of pure TiO_2 is average 200 nm. When FESEM pictures were examined and particle sizes were calculated, it was found that it was related to the crystal sizes calculated from XRD patterns.

While agglomerations were observed in the particles of TiO_2 synthesized without the addition of surfactant, it was not observed in those with surfactant added. Considering the homogeneity according to the variety of surface materials, the most homogeneous distribution was observed in TiO_2, which was synthesized by adding triton x. In addition, the most porous structure was observed in the sample in which CTAB was added.

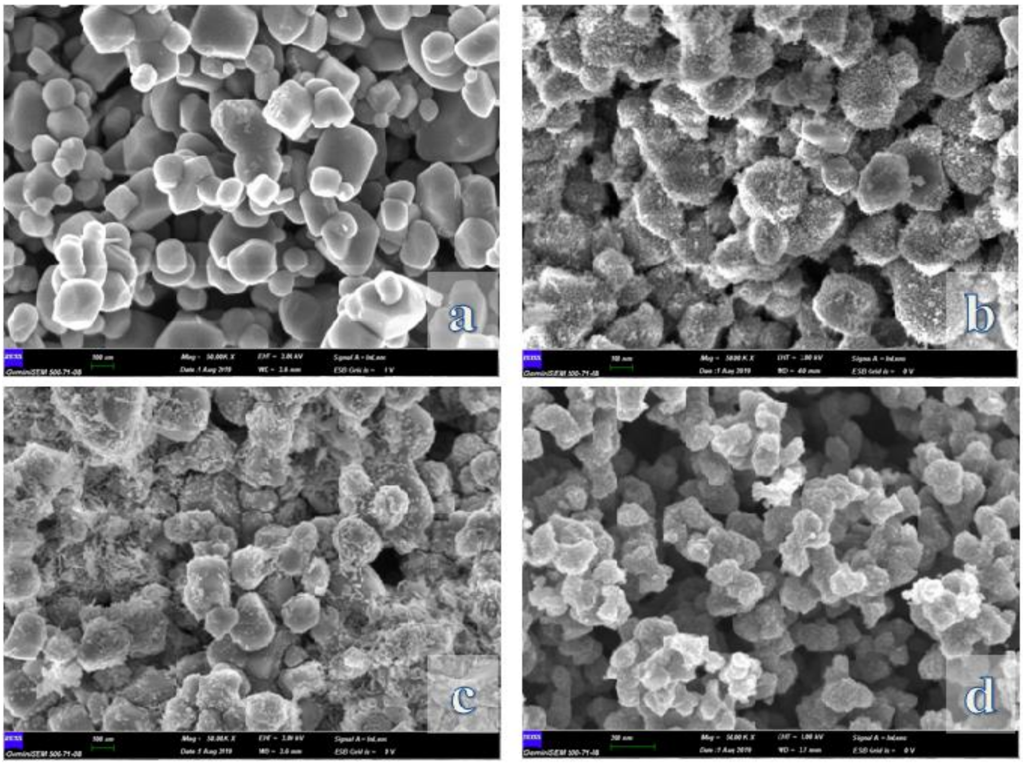

Figure 4. FESEM images of a) pure TiO_2 b) TiO_2+ sodium dodecyl sulfate (SDS) c) TiO_2+cetyl trimethyl ammonium bromide (CTAB), and d) TiO_2+nonionic (TritonX-100).

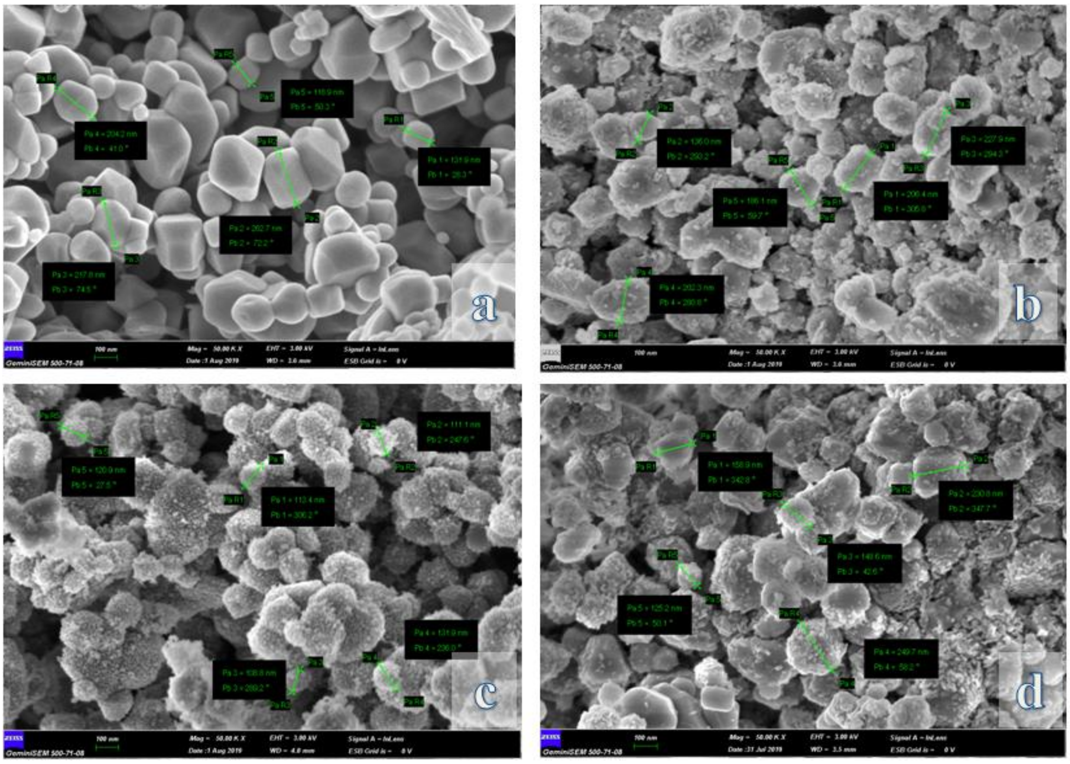

Figure 5. Particle size representation of a) pure TiO_2 b) TiO_2+ sodium dodecyl sulfate (SDS) c) TiO_2+cetyl trimethyl ammonium bromide (CTAB), and d) TiO_2+nonionic (TritonX-100).

These results could significantly contribute to all other studies with TiO_2. Structural changes of samples synthesized by the influence of surfactants include two aspects. On the one hand, the surface area of nanocomposites increases, which plays an important role in increasing absorption. On the other hand, the porosity increases and this will be the light for many studies (Zhang et al., 1998; Xu et al., 1999; Maira et al.,2000; Stepanov,2012; Stevanovic et al.,2012).

3.4. Porosity—N_2 Adsorption/Desorption Analysis

The specific surface area was estimated by applying the Brunauer -Emmett-Teller (BET) equation to the experimental N_2 isotherms using a micromeritic-Gemini IV analyzer. 25 mg of each sample was degasificated for 5 h at 150°C, and nitrogen adsorption-desorption isotherm was analyzed through the BET method. When the isotherms given in Figure 6 and the pore size distributions obtained by BJH method are examined, the shape of the isotherms can be defined as type 3 with hysteresis loops (type H3) characteristic for mesoporous materials (Sing et al.,1985). They also show the mesoporous structure of the sponge-like porous powders, which are very clearly observed in FESEM images. The specific surface area of the samples varies from 60 to 120 m^2/g depending on the presence and type of surfactant.

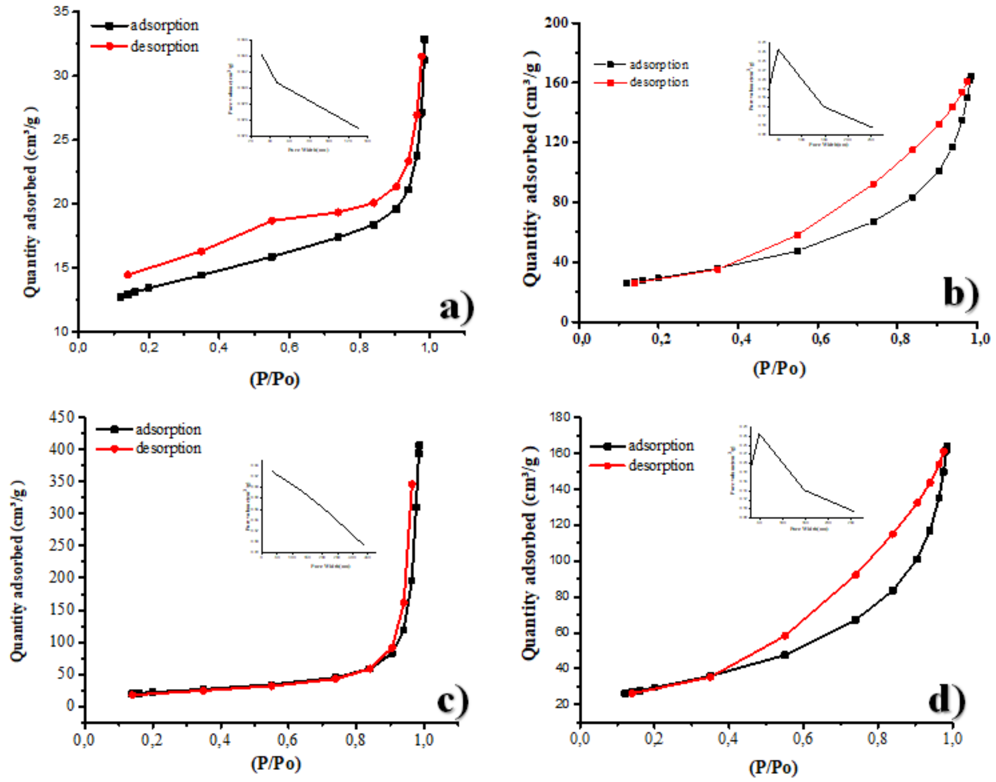

Figure 6. N_2 adsorption/desorption isotherms and pore size distribution of a) pure TiO_2 b) TiO_2+ sodium dodecyl sulfate (SDS) c) TiO_2+cetyl trimethyl ammonium bromide (CTAB), and d) TiO_2+nonionic (TritonX-100).

4.Conclusions

Here we have optimized the TiO_2 synthesis using different surfactants and as a result determined the most accurate surfactant ratio and the most effective surfactant. As a result of the analysis, TiO_2 synthesized by using 2.5% CTAB, both surface area and porosity were determined as the best material. In addition, in general, high surface area and porosity were found in materials synthesized with other surfactants. CTAB shows better dispersion and stability of TiO_2 than SDS and Triton X.

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