Removal of Cr(VI) from wastewater through glycine assisted synthesis of TiO$_2$

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Abstract: In this study, titanium dioxide was synthesized via solution combustion method. Titanium(IV) oxysulfate was used as a titanium source. The fuel type, reaction time, and reaction temperature were tested for optimization. The glycine was set as a suitable fuel. Structural properties of the final product were characterized by p-XRD. Scanning electron microscopy (SEM) and BET techniques were used to examine the morphology. The synthesized products were compared to the commercial TiO$_2$ and it was found that the titanium dioxide with the high surface area (63.628 m^2/g) has been successfully synthesized by solution combustion method with time and energy saving. In the second part of the study, the adsorption efficiencies of synthesized titanium dioxide were tested, removal of Cr(VI) from wastewater was carried out. It was found that titanium dioxide obtained via solution combustion method has a better capacity for Cr(VI) removal from wastewater than commercial titanium dioxide. In consequence, the chosen synthesis method modified the surface properties and improved the chromium adsorption capacity.

Key words: Cr(VI) adsorption, solution combustion method, titanium dioxide, titanium(IV) oxysulfate

1. Introduction

The titanium dioxide has several applications due to its excellent physical and chemical properties. TiO$_2$ has a broadband range (3.00 eV) and high refractive indices ($n \sim 2{,}3$), so it is frequently used in optical applications.[1] Because of its crystal structure and electronic structure, titanium dioxide is used in heterogeneous catalysis,[2] photocatalysis, and as a gas sensor.[3] In addition, due to the advantages such as high chemical stability, no toxicity, high catalytic activity, low cost, and easy production, titanium dioxide is the most used semiconductor in solar panels,[4] self-cleaning surfaces,[5] cancer treatments,[6] photovoltaic devices,[7] biomedical and environmental applications.[8] It is also used in sun creams as UV preservative,[9] as a white pigment in paints,[10] and in food industry.[11]

Various synthesis methods have been used to obtain titania such as sol-gel,[12] solvothermal method,[13] hydrothermal method,[14] microemulsion,[15] microwave method,[16] and combustion synthesis method.[17] The solution combustion method is widely used to synthesize oxides, nitrides, and carbides for thermal resistant oxides, dielectric materials, and insulators sensors. This technique depends on the exothermic redox reaction between a fuel and an oxidizer. In the recent years, because of its economic advantages, using simple equipment, short-term effect, and high purity product formation, solution combustion method has been used for titanium dioxide synthesis.[18]

Heavy metals such as Cd, Cu, Cr, Mn, Hg, Ni, Pb, Sn, Fe, and Zn are present in various industrial

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effluents. Heavy metals show toxic effects at high concentrations. One of the heavy metals that cause problems in terms of environmental pollution is chromium. Chromium exists in various concentrations in all biological materials. Chromium is found with $+6$ and $+3$ valences in wastewaters which is released from industries such as chrome plating, leather tanning, wood preservative production, stainless steel production, artificial fertilizer production, textile and pigment industries, copper processing, fire resistant brick production, glass industry, and photography.[19] Cr(VI) causes poisoning, respiratory sensitization and failure.[20] Therefore, different methods have been developed for the treatment of wastewaters containing Cr(VI). Many methods of remediation such as chemical precipitation,[21] ion exchange,[22] reverse osmosis,[23] adsorption,[24] and biosorption[25] are used to remove chromium from wastewater. From these methods, adsorption is seen as a powerful and versatile method to remove heavy metals when combined with appropriate desorption step solving the problem of sludge annihilation.

In the present study, anatase form of TiO_2 was successfully prepared by solution combustion synthesis using titanyl oxysulfate ($TiOSO_4$) as a titanium precursor and glycine (G) as a fuel source. Anatase is the most commonly used TiO_2 phase due to its superior properties such as homogeneous charge distribution, ease of electron-hole pair production, and photoconductivity.[26] The characterization of the structural and morphological properties of the synthesized products was examined. Adsorption characteristics of Cr(VI) ions from aqueous solutions on synthesized and commercial TiO_2 were investigated comparatively.

2. Results and discussion

2.1. Synthesis of TiO_2

2.1.1. Effects of fuel types

To determine the fuel type, which was the most important step for solution combustion method, G, citric acid (CA), oxalic dihydrazide (ODH), hexamethylenetetramine (HMTA), urea (U), and carbohydrazide (CH) were used as fuel. The structural characterization of the obtained products was performed using p-XRD. Figure 1 shows the XRD patterns of obtained products using different fuels.
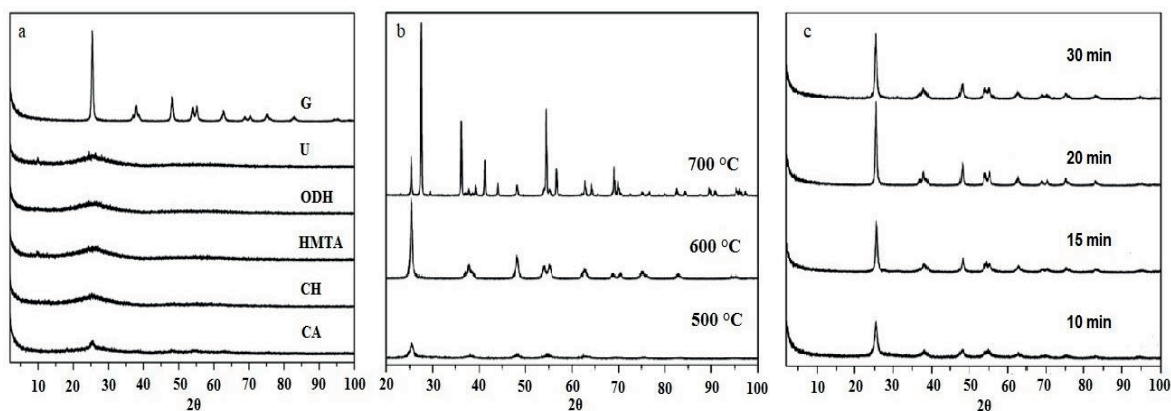

Figure 1. P-XRD patterns of products synthesized using a) different fuel types, b) different reaction temperatures, and c) different reaction times.

From p-XRD patterns, it was observed that the structures which were synthesized using CH, HMTA, ODH, and U, were amorphous. When CA was used as fuel, the reaction was considered to be incomplete even though titanium dioxide's $2\theta = 25.28°$ peak was observed. When G was used as fuel, the most intense peak of the anatase phase was observed at $2\theta = 25.28°$. In addition, the other peaks belonging to the a natase phase

were observed at $2\theta = 37.8°$, 48°, 53.9°, 54.8°, and 62.5° (JCPDS card no. 21-1272). As a result, it has been determined that the most suitable fuel is G for titanium dioxide synthesis from p-XRD analyses.

2.1.2. Effects of combustion temperatures

According to the combustion temperature analyses (Figure 1), titanium dioxide peaks were not fully formed at 500 °C. When the combustion temperature of the reaction was 600 °C, the characteristic peaks of the anatase phase of titanium dioxide were observed. When the combustion temperature was 700 °C, it was determined that the anatase phase turns into the rutile phase. In reaction time analyses at 600 °C (Figure 1), titanium dioxide was synthesized as anatase phase while the reaction time was 20 min. It has been observed that there was no significant change in the 2θ values of the peaks of the anatase phase when the reaction time was 30 min. After p-XRD analyses were completed, the reaction conditions were optimized as 600 °C, 20 min with G as the fuel.

2.2. Surface properties of TiO_2

In order to investigate and compare the surface properties of synthesized and commercial titanium dioxide, a surface analyzer (BET analysis) and scanning electron microscopy (SEM analysis) were used. According to the BET analyses, titanium dioxide synthesized by solution combustion method (63.628 m^2/g) has higher surface area than commercial titanium dioxide (11.347 m^2/g). It is believed that the intense gases released during combustion cause to increase the surface area of TiO_2.

The SEM images of the samples were shown in Figure 2. It was seen that the commercial titanium dioxide's anatase surface has a homogeneous and polyhedral structure, and the groups on the surface have been like clusters. The particle size of the titanium dioxide synthesized by solution combustion method was changed and increased 5–10 times compared to the commercial. It has been observed that the size distribution at the surface of titanium dioxide synthesized by solution combustion was not homogeneous, the surface had a more porous structure and the surface area was increased.
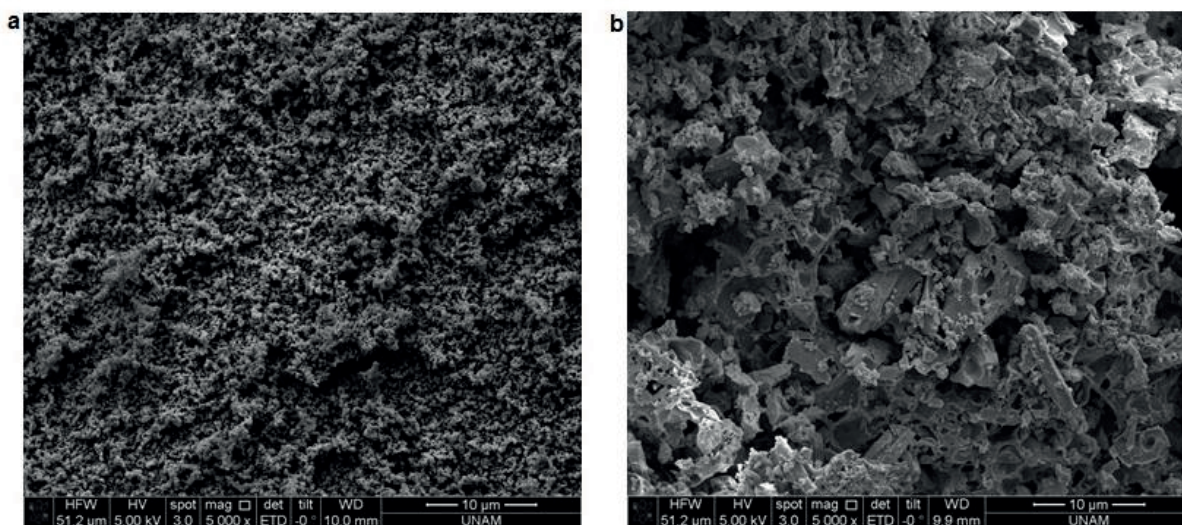

Figure 2. SEM images of commercial (a) and solution combustion synthesized TiO_2 (b).

2.3. Removal of Cr(VI) from wastewater

In the second part of study, Cr(VI) removal from wastewater was carried out by adsorption method. The synthesized and commercial titanium dioxide were used as adsorbents and the effects of parameters such as pH, adsorption time, initial Cr(VI) concentration, and adsorbent amount were investigated. In addition, isotherm and kinetic studies were carried out under optimum conditions.

One of the important parameters controlling the adsorption process was the pH. The change in the pH of the solution can cause effects such as hydrolysis, precipitation, redox reactions, and formation of the complex. As the hydronium (H_3O^+) and hydroxyl (OH^-) ions adsorb strongly on the adsorbent surface in aqueous media, the solution pH changes and other solution ions are affected by the solution pH. The effect of pH on adsorption amount was shown in Figure 3. The role of the hydrogen ion concentration has been investigated at different pH values from 2–10. The Cr(VI) concentration was fixed at 100 mg/L, the adsorbent amount was 100 mg, and the adsorption time was fixed at 60 min. The results show that the adsorption was the maximum at pH = 5.
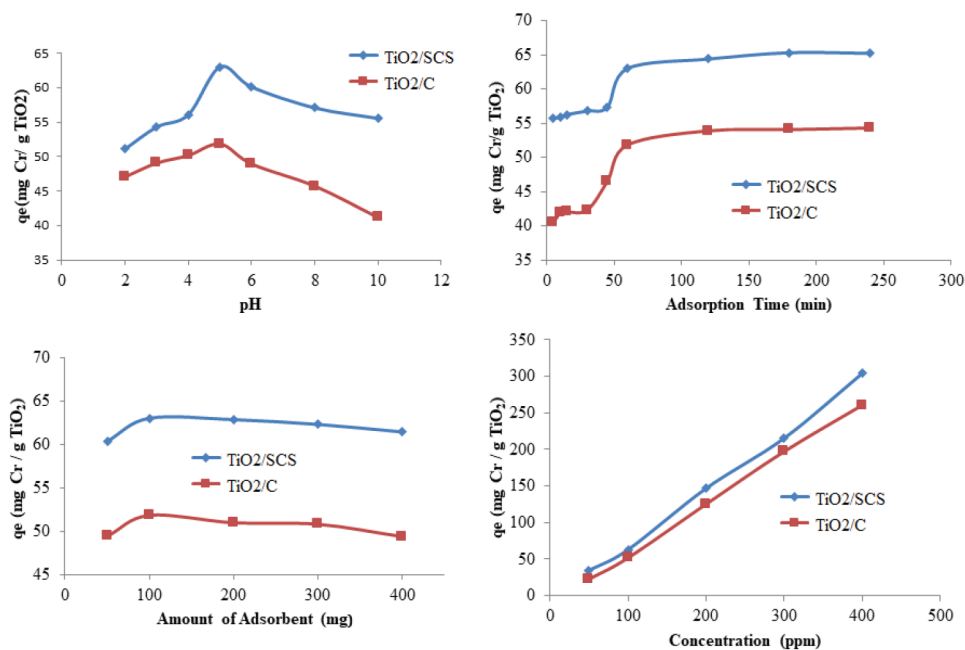

Figure 3. Effect of a) pH [Cr(VI) conc. = 100 mg/L, adsorbent amount = 100 mg, adsorption time = 60 min], b) adsorption time [Cr(VI) conc. = 100 mg/L, adsorbent amount = 100 mg, pH = 5], c) amount of adsorbent [Cr(VI) conc. = 100 mg/L, pH = 5, adsorption time = 60 min], and d) initial concentration [Adsorbent amount = 100 mg, pH = 5; adsorption time = 60 min].

The adsorption time was an important parameter for wastewater treatment. The effect of adsorption time on Cr(VI) adsorption was shown in Figure 3. The role of the adsorption time was examined at different times between 5 and 240 min. The results show that the maximum adsorption for both samples occurred within the first 60 min. After 60 min, the active sites of the adsorbent were filled with Cr(VI) ions, so it can be said that the adsorption has stabilized. Cimino et al.[27] reported that the removal efficiency of Cr(VI) increased with the contact time and after a certain period of time, Cr(VI) adsorption did not occur due to the active regions of the adsorbent reaching saturation.

The role of initial Cr(VI) concentration was investigated at different concentrations ranging from 50 to 400 mg/L. It has been found that the adsorption capacity increases with increasing metal concentration. This increase may be due to the interaction between the metal ions and the active centers of the adsorbent, and the adsorption capacity is increased by increasing the Cr(VI) concentration.

The effect of adsorbent amount was investigated with adsorbent amounts ranging from 50 to 400 mg (Figure 3). The obtained results showed that the adsorption was maximum when the amount of adsorbent was 100 mg. If the adsorbent had the capacity to adsorb metal ions in the environment, increasing the adsorbent dose did not affect the percentage of adsorption. In some cases, the removal rate can be reduced by increasing the amount of adsorbent. The reason of this was thought to be that the adsorbent particles adhered to each other and caused a decline in the surface area.

To investigate the adsorption process of Cr(VI), Langmuir and Freundlich isotherm models, the pseudo-first-order and pseudo-second order adsorption kinetics (Figure 4) were used.
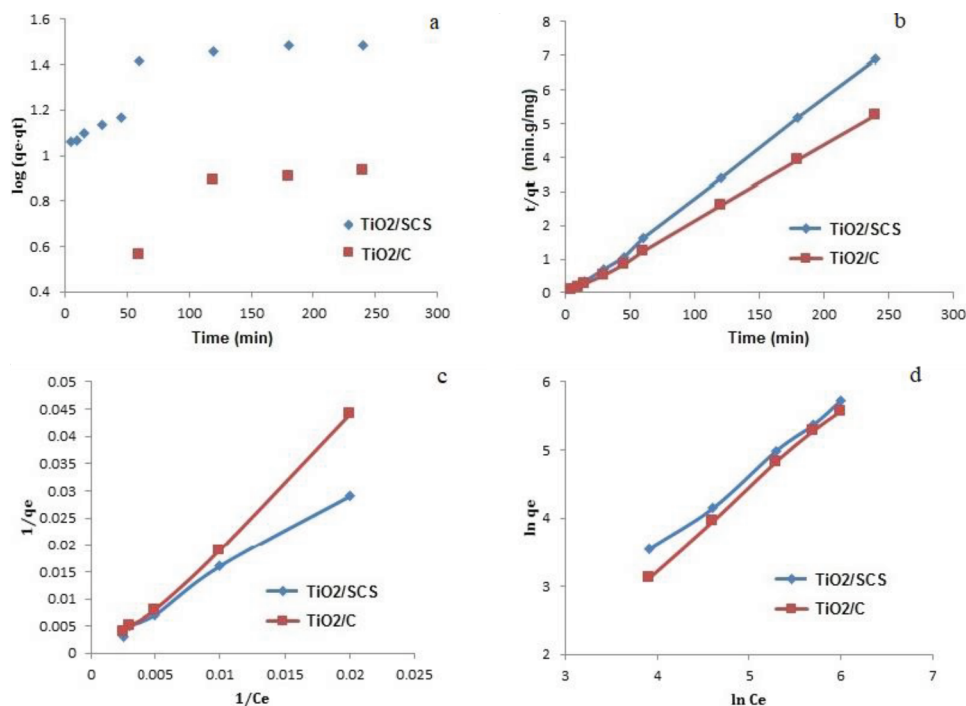

Figure 4. a) The pseudo-first-order and b) the pseudo-second order adsorption kinetics, c) Langmuir and d) Freundlich adsorption model for Cr(VI) adsorption.

Langmuir isotherm is used to describe single-layer adsorption. In the Langmuir isotherm, $1/q_e$ vs. $1/C_e$ values were plotted and the isotherm constants were calculated from the slopes, shifts, and given Eq. (1) (Table 1). Especially in heterogeneous adsorption systems, where monolayer adsorption occurs, Langmuir isotherm cannot clearly explain the equilibrium state. The dimensionless separation R_L constant was used to find the availability of adsorption is calculated using the Eq. (2).[28] The value of R_L indicates the nature of the adsorption process as $R_L > 1$-Unfavorable, $R_L = 1$-Linear, $0 < R_L < 1$-Favorable and $R_L = 0$-Irreversible. The Freundlich isotherm is used in particular to identify situations where the adsorption occurs in a multilayer and given in Eq. (3). In the Freundlich isotherm, $\ln C_e$ vs. $\ln q_e$ were plotted and the corresponding isotherm constants were calculated (Table 1).

Table 1. Langmuir and Freundlich adsorption model constants for solution combustion synthesized (SCS) and commercial (C) TiO$_2$.

Sample	Langmuir parameters				Freundlich parameters		
	q_{max} (mg/g)	b (L/mg)	R_L	R^2	K	n	R^2
TiO$_2$ /SCS	1000	0.00006	0.9940	0.9941	1.8875	0.9468	0.9964
TiO$_2$ / C	384.6	0.0011	0.9009	0.9961	4.5901	0.8401	0.9988

$$\frac{1}{q_e} = \frac{1}{b.q_{max} \cdot C_e} + \frac{1}{q_{max}} \tag{1}$$

$$R_L = \frac{1}{1 + b.Ci} \tag{2}$$

$$\ln q_e \ln K + \frac{1}{n} \ln C \tag{3}$$

q$_e$ is the amount of metal ions adsorbed per unit mass of adsorbent (mg/g); C$_e$ is the equilibrium concentration of the solute in the bulk solution (mg/L); q_{max} is the maximum adsorption capacity; C$_i$ is the initial concentration (mg/L); b is the Langmuir constant (g/L); K are the indicators of adsorption capacity, and n are the indicators of adsorption intensity.

R^2 values were compatible with both isotherms for the adsorption of Cr(VI). The higher regression coefficients obtained from Freundlich isotherm indicate that adsorption is better at Freundlich isotherms. The q$_{max}$ value is an indication of how many adsorbents can adsorb metal ions. According to the maximum adsorption capacities, it can be seen that TiO$_2$ /SCS can adsorb Cr(VI) more than commercial titanium dioxide. In addition, the RL separation factor is between $0 < RL < 1$, which means that adsorption is compatible.

The pseudo-first-order adsorption model (Eq. (4)) and the pseudo-second-order adsorption model (Eq. (5)) were applied to the experimental data to determine the adsorption mechanism. qe and qt are amounts of chromium adsorbed at equilibrium and time t (mg/g). k is the equilibrium rate constant of pseudo-first-order (min^{-1}). The initial sorption rate h $=$ kq$_e^2$ (mg/g.min) and k is the pseudo-second-order rate constant (g/mg min). Figure 4 shows the Cr(VI) adsorption kinetics and kinetic coefficients were given in Table 2. As a result of the kinetic study and the regression coefficients (R^2), the adsorption kinetics for both adsorbents are suited to the pseudo-second-order kinetics. This indicated that the kinetic behavior of TiO$_2$ is chemisorption with the rate-controlling step.[29]

Table 2. The pseudo-first-order and the pseudo-second-order kinetic coefficients.

Sample	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	qe	k	R^2	qe	k	R^2
TiO$_2$/SCS	12.785	4.606×10^{-3}	0.7625	34.246	6.915×10^{-3}	0.9992
TiO$_2$/C	3.459	4.376×10^{-3}	0.6974	45.045	5.737×10^{-3}	0.9995

$$\log(q_e.q_t) = \log q_e - \frac{k}{2.303}t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{5}$$

In order to investigate the reusability of solution combustion synthesized titanium dioxide as an adsorbent, the same sample was used three times. The qe values changed as 62.87 (first use), 60.47 (second use), and 49.54 (third use). The amount of adsorbed Cr(VI) showed a tendency to decrease in the third use while it varied in the first and second use. These results showed that, in addition to washing and drying processes, calcination processes can be required.

The Langmuir adsorption capacities (q_{max}) of the different adsorbents used for Cr(VI) removal were given in Table 3. When the Langmuir adsorption capacities of different adsorbents are compared, solution combustion synthesized TiO_2 can be considered a good adsorbent for Cr(VI) adsorption.

Table 3. Comparison of Langmuir adsorption capacities of various adsorbents for Cr(VI).

Adsorbent (mg/g)	q_{max}	Ref.
m-poly (EGD VPBA)	816.8	[30]
$MnO_2/Fe_3O_4/o$-MWCNT	186.9	[31]
Polypyrrole graphane oxide	625	[32]
Ti-Kitosan	171	[33]
Lanthanum diethanolamin	357.1	[34]
Turkish vermiculite	87.7	[35]
C. virgatum (red algae)	26.5	[36]
TiO_2/C	384.6	This study
TiO_2/SCS	1000	This study

2.4. Conclusions

Titanium dioxide was successfully synthesized via solution combustion method. U, CH, G, CA, HMTA, and ODH were used as the fuel type. It has been determined that the most suitable fuel is G. The p-XRD analyzes showed that the synthesized and commercial titanium dioxides were structurally identical. Experiments were carried out under optimized conditions (adsorbent amount = 100 mg, pH = 5, adsorption time = 60 min) and the obtained data were applied to Langmuir and Freundlich isotherms. The regression coefficients (R^2), which indicate the suitability of the data for isotherms, are shown to be compatible at both isotherms. Both adsorbents are better suited to the pseudo-second-order kinetic. When the velocity constants of both adsorbents are compared, the highest k rate constant is found for the titanium dioxide synthesized by the solution combustion method. As a result of adsorption studies, it has been determined that the titanium dioxide synthesized by the solution combustion method has more Cr(VI) removal capacity than commercial titanium dioxide.

3. Experimental

3.1. Instruments and chemicals

Titanium oxysulfate (Sigma, 99%), CH (Aldrich, 98%), U (Fischer, 99%), G (Merck, 99.7%), HMTA (Merck 99%), ODH (Sigma, 99.5%), nitric acid (Riedel, 65%), orthophosphoric acid (Analar, 99%), potassium dichro-

mate (Analar, 99%), sulfuric acid (Fluka, 95%–97%), sodium hydroxide (Riedel, 95%) and 1,5-diphenylcarbazide (Merck). were used without any purification.

Structural analyses of the products were carried out using Cu Kα composition ($\lambda = 1.5418$ Å) in powder X-ray diffractometer. Measurements were taken at $2\theta = 0°$–$100°$ on a Rigaku DMAX-2200 diffractometer. Morphological analyses of the products were performed using SEM and a BET analysis. SEM images were taken at a voltage of 12–24 kV and a current of 130–150 pA using a Quanta 200 FEG device. The surface areas were measured using a Quantachrome Quadrasorb SI Automated surface area analyzer after 6 h of degassing at 300 °C. Cr(VI) adsorption measurements using synthesized and commercial titanium dioxide were performed with a Perkin Elmer T80+ UV/VIS Spectrometer PG Instruments.

3.2. Synthesis

For optimization studies of synthesis parameters such as fuel type, synthesis temperature, and synthesis time have been carried out in order to synthesize titanium dioxide by solution combustion method. $TiOSO_4$ was used as the titanium source. The CH, U, G, HMTA, CA, and ODH were used as the organic fuel. The fuel/oxidizer ratio for each type of fuel was calculated according to the propellant chemistry and the stoichiometric fuel solutions were prepared.[37] The mixture prepared by adjusting the Ti/fuel molar ratios according to the propellant chemistry was dissolved in 5 mL of water and mixed with the magnetic stirrer. As a result of the calculation, the fuel/oxidizer ratios were set at 0.88 (G), 1.33 (U), 1.0 (CH), 0.22 (HMTA), 0.44 (CA), and 0.8 (ODH). The resulting mixture was dried at 100 °C. Dry material was burned at different reaction temperatures (500 °C, 600 °C, 700 °C) and time (10 min, 15 min, 20 min, 30 min).

3.3. Adsorption studies

One thousand ppm stock Cr(VI) solution was prepared using $K_2Cr_2O_7$. To measure the absorbance of the Cr(VI) solutions by UV-spectrophotometer, 1 mL of 1,5-diphenylcarbazide and 1 mL of 70% phosphoric acid were added to 1 mL of Cr(VI) solution and the solution volume was completed to 100 mL. The absorbance was read at 540 nm. Adsorption efficiencies were calculated from the obtained data. Langmuir and Freundlich isotherms were plotted for each adsorbent to determine which isotherm was more suitable.

To prepare the diphenylcarbazide solution, 250 mg of diphenylcarbazide was dissolved in 50 mL of acetone. It was stocked in a brown bottle and the usage time was 14 days.

In the study, optimization studies such as solution pH (2, 4, 6, 8, and 10), adsorption time (5 to 240 min), Cr(VI) concentration (50–400 mg/L) and adsorbent amount (50–400 mg) were done. The pH was calibrated using 0.05 M H_2SO_4 and 0.05 M NaOH. The obtained data were applied to adsorption isotherms and findings of the adsorption capacity and mechanism were revealed.

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