TiO₂ MODIFIED WITH CARBONIZED MATERIALS: PHOTOCATALYSIS/ ADSORPTION OF ORGANIC POLLUTANTS FROM AQUEOUS SOLUTION: A SHORT REVIEW

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The TiO₂/carbonized materials in composites provide a synergistic effect of adsorption and photocatalysis. The activated carbon or carbonized material can be prepared using various raw materials that present agricultural waste. The most commonly used process for the preparation of the activated carbon (AC)/carbonized material is chemical activation. Chemical activation produces the activated carbon with a good surface area and pore system, which contributes to better adsorption of organic pollutants. The TiO₂/AC composite materials can be prepared by sol-gel, hydrothermal and metal organic chemical vapor deposition (MOCVD) techniques. The most commonly used techniques for characterization of the TiO₂/AC materials are XRD, BET, TG Analysis and UV-Vis DRS, and will therefore be discussed in this paper. The TiO₂/AC composite materials have shown significant efficiency in removal of organic pollutants from aqueous solutions. The adsorption process of organic pollutants can be affected by various process parameters that will be observed in this paper.

Keywords: activated carbon, adsorption, carbonized materials, composite materials, TiO₂, photocatalysis

Introduction

Water pollution and increased use of clean water resources are major global problems that create the need for new and effective methods for water purification. Colors/dyes and non-biodegradable trace organics are one of the most threatening pollutants, due to industrial development. Adsorption by activated carbon (AC) is an effective method for the removal of organic compounds, from municipal and industrial waste water [1, 2]. The main disadvantage of AC usage is the fact that saturated AC has to be regenerated before reuse [1]. Also, after water treatment by using the AC, it may need to be treated as hazardous waste [1, 3]. There are several possible methods for AC regeneration that are based on desorption (which is induced by thermal treatment or displacement of solvent) and decomposition (which is induced by several processes: thermal, chemical, electrochemical and microbial) [3]. Photocatalytic regeneration is one of the catalyst regeneration processes used for regeneration of AC. TiO₂, SnO₂ and ZrO₂ are most commonly used semiconductor materials in photocatalytic regeneration. These semiconductor materials are organized in layers or impregnated on AC and irradiated with UV or solar light in order to generate high reactive species [3]. Heterogeneous photocatalysis presents an attractive solution for treatment of spent carbon, due to effective degradation of various organic contaminants at ambient conditions. In recent years, heterogeneous catalysis has found great

application in environmental clean-up. In photocatalytic reactions, along with the destruction of organic adsorbates, the regeneration of spent AC occurs as well [1].

Heterogeneous photocatalysis shows several advantages in comparison with other methods used for AC regeneration. These advantages are: 1) It can eliminate various organic pollutants; 2) There is no need for post treatment due to mineralization of organic adsorbates (final products of mineralization are non-toxic compounds such as H₂O, CO₂ and mineral acid); 3) Heterogeneous photocatalysis can be performed at low temperature and under solar radiation; 4) It provides simultaneous regeneration of activated carbon and destruction of organic adsorbates; 5) Smaller loss of activated carbon compared to the thermal regeneration, due to the absence of carbon burn off at elevated temperatures. In order to improve efficiency, in terms of energy consumption, heterogeneous photocatalysis has been combined with ultra-sound or chemical reagents such as H₂O₂ [1].

Over the last 20 years, interest in the application of heterogeneous photocatalysis by using TiO₂ nanopowders for the removal of organic hazardous compounds has grown [4,5]. The photodegradation process of organic pollutants by TiO₂ starts with the absorption of UV light that has energy equal or higher than the band gap energy (3.2 eV and 3.0 eV for TiO₂ anatase and rutile, respectively) [6].

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TiO₂ presents leading photocatalyst for water treatments due to its good photoactivity, high chemical and biological stability, low toxicity and relatively low cost. On the other hand, there are several disadvantages that may manifest while using TiO₂-based nanopowders; namely, they can easily agglomerate but can be difficult for recycling or for separation from the solution. [7,8]. In order to overcome these limitations, different support materials that provide large pore structure for TiO₂ dispersion, such as zeolite, alumina, silica, glass, carbon nanotube and activated carbon have been used [7,9-14]. Several criteria have been established for optimal catalyst support: 1) Material that is used as a support for the TiO₂ photocatalyst should be transparent or should allow passing of UV radiation; 2) Supporting material should be chemically inert; 3) Supporting material should bond physically or chemically with TiO₂, without effect on TiO₂ reactivity; 4) Supporting material should have large specific surface area and high adsorption affinity towards pollutants; 5) Supporting material should deliver fast and simple photocatalytic recovery and re-use. According to these criteria, activated carbon is good supporting material [6]. Coating TiO₂ particles on the surface of the AC combines benefits of these methods [1,15]. The AC acts as support of the TiO₂-based nanopowder catalysts and provides high concentration of pollutants and corresponding intermediates near the TiO₂ particles/surface, which leads to photocatalytic degradation of pollutants, providing in situ regeneration of the AC [1].

Activated carbon

Activated carbon (AC) presents a group of materials that are very effective adsorbents due to high surface area (that can reach 3000 m² · g⁻¹) and porosity, changeable surface chemistry and very good surface reactivity [16]. Due to these characteristics, the AC has been studied as an adsorbent, catalyst and catalyst support that can be used for the removal of different pollutants in both liquid and gas phase, and also for the purification and recovery of chemicals [16]. AC shows the amorphous structure that contains macro- (> 25 nm), meso- (1-25 nm) and micropores (< 1 nm) [17]. Activated carbon is derived from raw materials that should be low-cost and abundant, have a high content of carbon and low inorganic content, be activated easily and have a low degradation rate over the years [16].

Preparation and activation of activated carbon (AC)

In practice, the two most used precursors for activated carbon preparation are coal and agricultural by-products [18]. Coal is more often used than agricultural by-products due to its low price and good supply [16], but in some cases it is better to use agricultural by-products [18]. Frequently used lignocellulosic materials or agricultural waste for AC preparation are peat, wood (cassava peel, resak wood, tamarind wood), nutshells (coconut nutshell, walnut shell), rice husk, etc. [6,19-26].

Preparation of activated carbon can be derived in two main stages. The first stage is the carbonization of

raw material that includes drying, then heating in order to remove hydrocarbon by-products (tars, volatile organic compounds). The pyrolysis process is completed after heating material in temperature range of 500 – 700 °C in inert (nitrogen) [22] or self-generated atmosphere [25]. The activation process follows the carbonization process, where the carbonized material is exposed to an activating agent [6]. Activation of carbonized material can be obtained in two ways: by chemical or by physical activation. In chemical activation, carbonized material is activated by chemical agents. In physical activation, activating agents are CO₂ [27] or water vapor [20,27].

In comparison with physical activation, chemical activation shows two advantages: 1) Chemical activation can be accomplished in a single step [23]; 2) It occurs at a lower temperature, thus it can improve the development of pores and also carbon yields are higher due to the effect of the used chemicals [21,24]. Chemical activation can be performed in the presence of chemicals such as: KOH [19,24,28], NaOH [22,26,29] and H₂SO₄ [21,23]. A possible mechanism of chemical activation is shown in Figure 1 [19].

Figure 1. Carbon activation mechanism [19].

Among the basic activating agents, NaOH shows following/numerous benefits in comparison with KOH: 1) Lower dosage of NaOH-activated carbon in comparison with the dosage for KOH-activated carbon; 2) NaOH is less corrosive; 3) NaOH has a lower price; 4) NaOH is more environmentally friendly compared to KOH [29]. Sulphuric acid, known for its dehydration capability, is widely used for the preparation of activated carbon. Chemical activation by H₂SO₄ improves pore development and provides high yields of carbon [21].

Sudaryanto et al. [24] prepared activated carbon from cassava peel using chemical activation with KOH. In order to achieve optimal parameters for the production of activated carbon with high surface area, various parameters were observed (different carbonization time, temperatures and impregnation ratios). Chemical activation was performed by mixing the defined amount of cassava peel with KOH solution at 50 °C for 3 h. The applied impregnation ratios of KOH to cassava peel were in the range from 1:2 to 5:2 (mass basis). After that, the prepared samples were dried at 110 °C for 24 h, and then carbonized in a horizontal tubular furnace at following temperatures: 450 °C, 550 °C, 650 °C and 750 °C. Processes of activation and carbonization were performed

in nitrogen atmosphere. Carbonization time was 1, 2 and 3 hours. After that, samples were cooled down under nitrogen atmosphere. The activated carbon samples were washed with 0.5M HCl and subsequently with hot distilled water until the pH of the solution reached 6.5. Samples were finally washed with cold distilled water. In the end, samples were dried at 110 °C for 24 h. Sudaryanto et al. [24] reported that carbonization time does not have much effect on a BET surface area of activated carbon. On the other side, increasing the carbonization temperature from 450 to 700 °C, showed significant improvement in pore development and formation of new pores. At temperatures higher than 400 °C, the reaction that occurs between KOH and C was (eq. 1) [24]:

Impregnation ratio was one of the most important parameters in the chemical activation process that affected the pore structure of activated carbon. It can be noted that at low impregnation ratio (50%) micropores were mainly present in the porous structure of AC. With the increase of impregnation ratio the formation of micropores increased and this also affected the widening of micropores to mesopores. The yield of activated carbon decreased with increasing impregnation ratio [24].

Cazzeta et al. [22] prepared activated carbon from coconut shell using two-step activation processes with NaOH as activating agent. Raw material, with particle sizes between 250 and 420 µm, was placed in a horizontal stainless steel reactor and heated from room temperature to 500 °C for 2 h. After that, prepared char was mixed with varying amounts of NaOH pellets and constant amount of water at ratios 1:1, 2:1 and 3:1 (NaOH : char) in a vertical stainless steel reactor. Samples were stirred for 2 h then heated at 130 °C for 4 h. After that, dry mixture was transported into a furnace and heated at 700 °C for 1.5 h in N₂ atmosphere. Afterwards, cooled samples of activated carbon were washed with 0.1M solution of HCl, followed by washing with hot distilled water until pH solution reached approximately 6.5. During the washing step, activated carbon was separated with 0.45 µm membrane filters. In the end, samples were dried at 110 °C for 24 h. Cazzeta et al. [22] reported that usage of NaOH as activating agent provided the material with high surface area and developed pore structure (with different sizes of pores) [22]. Greater impregnation ratio NaOH : char implied an increase in surface area and a decrease of carbon yield. The activation mechanism with NaOH is given by the following formula (eq. 2) [22]:

Karagoz et al. [23] prepared activated carbons from waste biomass (sunflower oil cake) using sulfuric acid. Waste biomass was treated with a solution of sulfuric acid and stirred for 24 h under continuous agitation. In order to prepare impregnated sample, the mixture was

dried at 110 °C for 24 h. The impregnated sample was transferred into a stainless steel reactor. After that, the sample was carbonized at 600 °C in nitrogen atmosphere. After cooling down, the prepared sample was washed with hot water then with cold water, until the solution was neutral. Finally, the sample was dried at 110 °C for 24 h in order to prepare activated carbon. Impregnation ratios were 0.0, 0.85 and 1.90, and corresponding carbonized materials samples were denoted as AC1, AC2, and AC3, respectively. Experimental results suggested that impregnation ratio strongly affected the characteristic of activated carbon. The greatest surface area of activated carbon was reported for the impregnation ratio 0.85.

Synthesis of TiO₂/AC

Various techniques for the synthesis of TiO₂/AC materials have been used. These techniques can be separated into two main groups: 1) chemical methods (sol-gel, hydrothermal, chemical vapor deposition, binders, molecular adsorption-deposition) and 2) physical methods (ionized cluster beam) [30]. In this paper, sol-gel [31-33], hydrothermal [34,35] and metal organic chemical vapor deposition (MOCVD) [36,37] will be discussed.

Wang et al. [33] prepared TiO₂/AC composites via acid-catalyzed sol-gel method. Ti(OC₃H₇)₄ was used as the precursor, and nitric acid was used as acid catalyst. A certain amount of AC (20, 50 and 80 wt.%) was added to Ti(OC₃H₇)₄ ethanol solution. The mixture was constantly stirred until the formation of gel. After that the formed gel was aged, then grounded and dried at room temperature. The prepared TiO₂/AC composites were calcined at 300, 450 and 600 °C for 2 h in flow of air [33].

Wang et al. [34] applied the hydrothermal method for synthesis of TiO₂/AC composite materials. Metatitanic acid (H₂TiO₃) was used as a precursor. Peroxotitanate was prepared by adding H₂TiO₃ to the solution that contained H₂O, H₂O₂ and NH₄OH. In order to prepare the homogenous solution, the solution was stirred for one hour. Granular AC (0.15 – 0.25 mm) was added to the solution. After stirring for 12 h, the samples were moved to Teflon reactor and heated for 8 h at 180 °C. Hydrothermally prepared samples were dried for 2 h at 120 °C and calcined for 2 h at 300 – 800 °C [34].

In general, chemical vapor deposition (CVD) is an industrial chemical process, which uses various techniques for deposition in order to form thin films from diverse precursors on substrates (common semiconductor materials). During the CVD process, the substrate is exposed to a single or multi component gaseous precursors in an inert atmosphere, under conditions of controlled high temperature and pressure. In the preparation of TiO₂-based materials supported on AC applying chemical vapor deposition, most researchers select metal organic chemical vapor deposition (MOCVD). This preference is due to metallo-(organic/inorganic) precursors and activated carbon as a support material [6]. Table 1 presents a short review of synthesis techniques, synthesis conditions and BET surface area of TiO₂/AC

composite materials.

In recent times, a lot of attention has been focused on MOCVD, as a method for the synthesis of AC supported TiO_2 catalysts. The reason for this is due to several advantages of MOCVD technique: 1) it has little effect on porous structure of the supported material; 2) the elimination of the traditional steps in synthesis (saturation, drying and reduction); 3) material properties are easily controlled. The apparatus of MOCVD technique is shown in Figure 2. High loading of TiO_2 on AC surface provides high catalytic activity. In order to achieve high loading of TiO_2 on AC surface, a long deposition time is required, which represents a disadvantage of this method. The long deposition time can affect the texture of AC, flow of carrier gas and it demands high energy consumption. Contrarily, high loading of TiO_2 on AC surface can cause agglomeration of particles and decrease catalytic activity of TiO_2/AC materials [37]. MOCVD is a gas phase synthesis technique. Applied gaseous precursors in MOCVD can easily enter into the pores of AC which results in the production of TiO_2 particles that are located in the interior volume of AC porous system. This does not contribute to photocatalytic reaction due to the fact that only the TiO_2 particles that are on the surface of AC can be excited by light. Numerous studies imply that oxygen carrying groups on the AC surface are main anchoring sites for TiO_2 precursor. There is a good chance that if a large concentration of the oxygen carrying group is present on AC surface, the precursor will be anchored in large amounts on the external surface of the AC in order to increase the external concentration of deposited TiO_2 on the AC using MOCVD technique [36]. Modification of AC using an acid treatment such as HNO_3 is an efficient way of improving the mesopores surface area and quantity of oxygen carrying groups on the surface of AC. Acid treatment of AC can improve deposition rate of TiO_2 on AC external surface by MOCVD. Also, enhanced concentration of oxygen carrying groups and high mesopores surface provide high catalytic activity due to well dispersed smaller-sized particles [37].

Figure 2. Schematic diagram of MOCVD system [36].

Zhang et al. [37] prepared activated carbon supported TiO_2 -based photocatalysts using the MOCVD technique. They explored the effects of HNO_3 modification

on activated carbon. Oxidation of AC samples (50 – 80 mesh) was performed by boiling AC in HNO_3 with different concentrations (1 – 15 mol/l), at 373 K for 1 h. After oxidation treatment, AC samples were washed with distilled water. A fixed amount of AC was set in quartz reactor, where the dehydration process occurred in nitrogen steam for 3 h at 573 K. Then, the reactor temperature was increased to 873 K. After temperature stabilization in the reactor, the deposition of the TiO_2 was initiated by switching tetrabutyltitanate (TBOT) with a N_2 flow. The gas line with flow rate of 400 ml/min was heated, in order to evade the precursor condensation. After transportation into the reactor, TBOT decomposed and formed TiO_2 particles. The deposition process lasted between 6 – 24 hours.

Table 1. Short review of synthesis techniques, synthesis conditions and BET surface area of TiO_2/AC composite materials [31-37]

Methods of TiO_2/AC synthesis	Precursor	Type of AC	Synthesis condition	BET surface for TiO_2/AC (m^2/g)	References
Sol – gel	TBOT	Commercial AC grains JSYX33	Annealing: 250°C for 2 h in air Calcination: 300 – 700°C for 2 h in N_2 atmosphere	237 – 293	[31]
Sol – gel	TBOT	Commercial AC grains JSYX33	Annealing: 250°C for 2 h in air Calcination: 300 – 700 °C 2 h in N_2 atmosphere	271 – 478	[32]
Modified sol-gel	TTIP	Commercial AC 100 mesh	Calcination: 300 – 600°C for 2 h in flow of air	5 – 427	[33]
Hydrothermal	Metatitanic acid	Coconut shell AC (0.15 – 0.25 mm)	Stirring: 12 h Teflon reactor: 180°C for 8 h Drying: 120°C for 2 h Calcination: 300 – 800°C for 2 h	959 – 1060	[34]
Hydrothermal	TTC	Commercial AC	Stirring for 30 min Heating: 98°C for 1 h Adjusting pH of solution (pH 8) Heating at 98°C for 1 h Aging at room temperature for 10 h Drying at vacuum at 70°C for 24 h Heating to 500°C for 2 h in N_2 atmosphere Heating: 2 h 500°C in N_2 atmosphere	67.56 296.35	[35]
Metal organic chemical vapor deposition	TBOT	Commercial AC (50 – 80 mesh) Treated with: HNO_3 , H_2O_2 and $\text{N}_2 + \text{O}_2$	Deposition temperature 873 K Source temperature: 423 K N_2 flow rate: 400 ml/min	/	[36]
Metal organic chemical vapor deposition	TBOT	Commercial AC (50 – 80 mesh) Treated with HNO_3	Deposition temperature: 873 K N_2 flow rate: 400 ml/min	/	[37]

Proposed mechanism of pollutants degradation using TiO_2/AC composite materials prepared by MOCVD and/or sol-gel method

The traditional methods used for synthesis of supported catalysts are wet impregnation, precipitation and sol-gel methods. In recent times, metal organic chemical deposition (MOCVD) found extensive use in the preparation of activated carbon supported materials. The process of MOCVD technique is continuous with the ability to easily control process parameters. Also, it is relatively

low-cost and requires simple apparatus [6]. The TiO_2 coating by MOCVD showed good adhesion on AC surface and the activated carbon supported TiO_2 -based photocatalyst provided a better activity for degradation/mineralization of pollutants compared to the powder TiO_2 photocatalyst (Degussa P25) [37]. MOCVD is a gas phase preparation method, which provides easy access for precursors to the AC surface. As a result, the deposited TiO_2 on the surface of AC forms a TiO_2 + AC hybrid film [5].

Figure 3 shows a proposed mechanism of pollutants degradation with composite TiO_2/AC materials prepared via MOCVD and sol-gel method. When TiO_2/AC composite prepared by MOCVD was used, the intermediates that were produced during the degradation of methyl orange (MO) could easily be adsorbed by TiO_2 + AC hybrid film. This would prevent the release of intermediates in the solution and provide their mineralization which would result in a significant decrease of Total Organic Carbon (TOC) of the solution. On the other hand, in case of TiO_2/AC material synthesized by sol-gel method, the photocatalytic reaction occurred mainly on the TiO_2 film, so intermediates could easily suspend into the solution. Suspended intermediates could only be further degraded if they were additionally collided with photocatalyst [5].

Figure 3. Schematic proposed of degradation of pollutants with TiO_2/AC catalysts prepared by different methods [5].

In situ regeneration of TiO_2/AC adsorbent

Zhu et al. [1] study compared regeneration efficiency of spent TiO_2/AC after dye removal treatment of color, using photocatalytic regeneration only by UV irradiation, combined with ultra-sound and combined with H_2O_2 . Experiment results showed that photocatalytic process was efficient in the removal of absorbed pollutant and regeneration of spent TiO_2/AC adsorbent, but efficiency was notably improved in combination with ultra-sound or H_2O_2 . The optimal time to accomplish regeneration of spent TiO_2/AC adsorbent was 16 h, under UV irradiation. Under the same conditions, in the presence of H_2O_2 , the irradiation time needed to achieve the same level of regeneration of spent TiO_2/AC adsorbent was reduced to 3 – 4 hours. This happened due to the fact, that under UV irradiation the addition of H_2O_2 can significantly increase the generation of free radicals and therefore promote a

photocatalytic reaction. Using a combination of UV irradiation and ultra-sound, the regeneration time of spent TiO_2/AC after color removal was 30 minutes. Significant improvement of regeneration efficiency may be associated with the sonophotocatalytic synergistic effect [1].

Characterization of TiO_2/AC composite materials

Various characterization techniques have been used to examine physical, mineralogical, photochemical and crystallo-chemical properties of TiO_2/AC composites. In this paper X-ray diffraction (XRD), BET surface, Thermogravimetric Analysis and UV-vis Diffuse Reflectance Spectroscopy (DRS) will be discussed.

XRD provides structural information for TiO_2/AC materials. The XRD technique can also give information about anti-calcination effect that is indicated by the presence of AC. Li et al. [31] reported that XRD results for sol-gel synthesized composites TiO_2/AC in comparison with bare TiO_2 (prepared in the same way and calcined at the same temperature) showed the presence of crystalline and amorphous phase. The presence of AC in composite TiO_2/AC increased the required temperature for anatase to rutile phase transformation. In comparison with bare TiO_2 materials, the average crystallite size of TiO_2/AC composite materials was smaller [31]. Wang et al. [33] also prepared TiO_2/AC composite materials via sol-gel method that contained 20, 50 and 80 wt.% AC. Wang et al. [33] reported that the average crystallite size of TiO_2/AC decreased with the increase of initial carbon content in composite materials, in comparison with bare TiO_2 for samples calcined at 300 °C. Contrarily, at 450 °C the average size of TiO_2/AC composite increased with the increase of initial carbon content and the average crystallite size of TiO_2/AC was larger in comparison with bare TiO_2 [33].

Figure 4. XRD patterns of samples prepared at different heat-treatment temperatures. (A) TiO_2/AC and (B) TiO_2 powders-(a) 300 °C-treated, (b) 400 °C-treated, (c) 500 °C-treated, (d) 600 °C-treated, (e) 700 °C-treated [31].

Wang et al. [33] reported that the increase in the BET surface area of TiO_2/AC samples calcined at 300 °C corresponded to amount (wt.%) of the activated carbon in TiO_2/AC composite materials. For sol-gel synthesized

composite materials specific surface area of TiO_2/AC significantly dropped with increasing temperature in calcination process. At the calcination temperature of 600°C , the values of BET surface area indicated the presence of non-porous texture [33].

Wang et al. [34] prepared TiO_2/AC composite materials by hydrothermal method. Composite materials contained 8% by weight of deposited TiO_2 on activated carbon. It was observed that for the sample treated at lower temperature, the presence of TiO_2 led to a decrease/reduction of the specific surface area of AC. At higher calcination temperatures (300°C and 400°C) the specific surface area of TiO_2/AC increased. This was attributed to desorption of NH_3 from the surface of AC, originated from NH_4OH used in synthesis. With further increase in calcination temperature (from 500 to 800°C), the specific surface area of TiO_2/AC decreased [34].

Figure 5 shows TG analysis of (a) bare TiO_2 and (b) TiO_2/AC composite material that contained 20 wt.% of AC [33]. DTG curve of TiO_2 (a) showed an intensive band at around 80°C that was attributed to the evaporation of alcohol solvent and broad band around 250°C which implied the destruction of TiO_2 -gel (indicating that the crystallization process occurred). TG curve of TiO_2 revealed mass loss of 29 wt.% and 1 wt.%, up to 400°C and 800°C , respectively. Figure 5 (b) TG and DTG curves of 20-AC- TiO_2 show two sequential mass losses that are attributed to the decomposition of titanium alkoxide and carbon. The noticeable mass loss for activated carbon was observed around 500°C [33].

Figure 5. TG analysis for different xerogel (a) TiO_2 and (b) 20-AC- TiO_2 [33].

The influence of carbon content on the band energy on TiO_2 can be observed in UV-Vis diffuse reflectance spectra (Figure 6). The absorption of the TiO_2/AC composites was very strong under 400 nm . Also, absorption in the visible area of spectra increased with the final carbon content in TiO_2/AC composite materials [33]. Liu et al. [35] reported that reflectance of the TiO_2/AC composites decreased in the range from 400 to 600 nm and pointed out that adsorption edges remained unchanged for TiO_2/AC composite materials. Furthermore, there were no significant changes in band gap energy [35].

Figure 6. Diffuse reflectance UV-vis spectra of TiO_2 -300, TiO_2 -450, 20-AC- TiO_2 -300 and 80-AC- TiO_2 -450 [33].

Application of AC

In 80% of its application, activated carbon is used for liquid phase transformation. The adsorption process is the result of the interaction between the surface of activated carbon and the adsorbate. These interactions can be electrostatic and non-electrostatic. Electrostatic interaction occurs if the adsorbate is an electrolyte that dissociates in aqueous phase. These interactions can be repulsive or attractive, which depends on: 1) the charge density of the AC surface; 2) adsorbate chemical properties; 3) ionic strength of the solution. Always attractive, non-electrostatic interactions include: 1) Van der Waals forces; 2) hydrogen bonds; 3) hydrophobic interaction [16]. Activated carbon shows strong affinity for hydrophobic and nonpolar compounds. It can be used for adsorption of pesticides, toxins, dyes, compounds that cause taste of water, etc. AC is also used as an adsorbent for polar and ionogenic organics, and for natural organic matter (NOM) as well [30]. The adsorption process of organic pollutants from aqueous solution can be affected by solution temperature, pH of the solution, initial concentration of organic pollutant, contact time between activated carbon and aqueous solution, etc.

Influence of various process parameters on adsorption process by activated carbon

The effect of pH

The pH of the solution is one of the most important

factors of pollutant (methylene blue) adsorption on the activated carbon surface because it controls electrostatic interactions between the adsorbent and the adsorbate. The increase of pH affects the surface properties of activated carbon. Figure 7 shows the effect of pH on the adsorption of methylene blue on activated carbons. The main parameter that influences adsorption of MB onto activated carbons is the pH of solution. In Figure 7, it can be noted that increasing the pH of the solution leads to a significant improvement of the adsorption process in pH area between 3 and 6. The increased pH value of the solution implied greater negative charge on the surface area of activated carbon, which results in better adsorption of positive molecules of methylene blue. In this case, maximum adsorption of MB with positive charge occurred at pH 6 [23].

Figure 7. Effect of pH for the adsorption of methylene blue onto the activated carbons [23].

The effect of temperature

The effect of temperature on the adsorption of MB on the activated carbon was observed for the temperatures between 15 and 45 °C. Experimental results confirmed that there is a correlation between adsorption and solution temperature. The magnitude of adsorption was proportional to the temperature of the solution. The maximum adsorption capacity for MB onto activated carbons was obtained at 25 °C [23].

The effect of the initial concentration of pollutant

In order to evaluate the effect of initial MB concentration on the adsorption process of MB on activated carbon, the range of initial MB concentrations used was 0 – 250 mgL⁻¹. Experimental results showed that the adsorption capacity of activated carbon increased along with the initial concentration of MB. This indicated that an increase in the initial concentration of MB delivers driving force that can overcome the mass transfer resistance between the solution and activated carbon. Maximum adsorption capacity was observed at the initial concentration of MB of 250 mgL⁻¹ [23].

The effect of contact time

To investigate the effect of contact time, the amount of adsorbed MB on the activated carbon versus time was

observed. Experiments were carried out under the same initial concentration of MB (25 ppm) and temperature (25 °C), in the time range 0 – 1140 min. At the beginning of adsorption, dye molecules reach the boundary layer and diffusion into the absorbance surface occurs after that. In the end, dye molecule diffuses into the pore structure of the adsorbent. This phenomenon requires longer contact time. The maximum adsorption capacity for MB adsorption on AC3 required longer contact time (1440 min), compared to AC1 and AC2 (900 min) [23].

Adsorption kinetics and isotherms

Kinetic mechanism of the adsorption process was investigated by testing the pseudo-first-order, pseudo-second-order, and intraparticle diffusion in order to present experimental data. For all activated carbon samples (AC1, AC2, AC3) kinetic mechanism of the MB adsorption well followed the pseudo-second-order rate model. Figure 8 shows that correlation coefficients for all samples were higher than 0.99 [23].

Figure 8. Pseudo-second-order kinetic plot for the adsorption of methylene blue onto the activated carbons [23].

The pseudo-second-order kinetic model is expressed as follows (eq.3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \dots \dots \dots (3)$$

where q_t is the amount of the dye adsorbed at time t , in mg g⁻¹, q_2 is the maximum adsorption capacity (mg g⁻¹) for the pseudo-second-order adsorption, k_2 is the equilibrium rate constant for the pseudo-second-order adsorption (g mg⁻¹ min⁻¹) [23].

The experimental data were tested using the linear forms of Langmuir and Freundlich isotherms. It was confirmed that for all activated carbon samples (AC1, AC2, AC3), adsorption behavior can be described using a monolayer Langmuir type isotherm (Figure 9) [23].

Figure 9. Langmuir plots for the adsorption of methylene blue onto the activated carbons [23].

Langmuir type isotherm is expressed as follows (eq.4):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (4)$$

where q_e is the equilibrium MB concentration on the activated carbon (mg g^{-1}), C_e is the equilibrium MB concentration in the solution (mg L^{-1}), q_{max} is the monolayer adsorption capacity of the activated carbon (mg g^{-1}), K_L is the Langmuir adsorption constant (L mg^{-1}) [23].

Conclusion

In comparison with TiO_2 and AC used separately, the TiO_2/AC composite materials showed advantages in the efficiency of pollutants degradation/mineralization. This is because on one hand, the presence of AC provides higher concentration of pollutants near the catalyst surface, while on the other hand, TiO_2 offers in situ regeneration of activated carbon. Efficient in situ regeneration of spent TiO_2/AC adsorbents used for color removal achieved after UV treatment combined with ultra-sound or H_2O_2 . Synthesis conditions such as: precursor/raw material, activating agent, impregnation ratio, carbonization time and carbonization temperature affect physico-chemical properties of the prepared activated carbon.

The MOCVD technique showed several advantages in comparison with hydrothermal and sol-gel synthesis methods. Also, the reaction mechanism that occurred in the case of TiO_2/AC synthesized via MOCVD, implied that these materials showed better performance in the adsorption and degradation/mineralization of pollutants and their intermediates.

The efficiency of the pollutant (methylene blue) removal from aqueous solution by the adsorption process on the activated carbon is influenced by pH, temperature, initial concentration and contact time. It was noted that pH was the key factor that influenced the process of adsorption of MB onto activated carbon. High initial concentration of pollutant implied faster and better adsorption capacity. Kinetic adsorption model for all samples of activated carbon followed pseudo-second-order ad-

sorption. The adsorption behavior of all activated carbon samples was well described by Langmuir type isotherm.

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Izvod

TiO₂ MODIFIKOVANA KARBONIZOVANIM MATERIJALIMA: FOTOKATALIZA/ADSORPCIJA ORGANSKIH POLUTANATA U VODI: KRATAK PREGLEDNI RAD

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Kompoziti TiO₂/karbonizovani materijal obezbeđuju sinergistički efekat adsorpcije i fotokatalize. Aktivni ugalj (AC) ili karbonizovani materijal može biti pripremljen iz različitih sirovih materijala kao što je poljoprivredni otpad. Najčešće korišćen postupak za pripremu aktivnog uglja je hemijska aktivacija. Hemijskom aktivacijom se dobija aktivni ugalj koji poseduje veliku specifičnu površinu i poroznu strukturu, koja doprinosi boljoj adsorpciji organskih polutanata. Kompozitni TiO₂/AC materijali se mogu sintetisati sol-gel, hidrotermalnom i MOCVD (metalo-organska hemijska depozicija parom) tehnikom. Najčešće primenjivane tehnike za karakterizaciju TiO₂/AC materijala su XRD, BET, DTG analiza i UV-Vis – DRS o kojima će biti diskutovano u ovom radu, na bazi literaturnih podataka. Kompozitni TiO₂/AC materijali su pokazali veliku efikasnost u uklanjanju organskih polutanata iz vodenih rastvora. Na adsorpcioni proces organskih polutanata na aktivnom uglju može uticati niz procesnih parametara o kojima će biti diskutovano u ovom radu.

Ključne reči: aktivni ugalj, adsorpcija, karbonizovani materijali, kompozitni materijali, TiO₂, fotokataliza