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ABSTRACT: Since phenol is toxic and yet its biologic reduction and removal is so difficult, strict limits are applied for the discharge of phenol-containing substances in the environment. Discharge of phenol-containing industries, sewages into natural waters is a serious threat to human health. In this study, the main objective is to consider the possibility of removing phenol with high initial concentration using a Heterogeneous Photocatalytic process. First, the absorbent SBA-15 and Graphene oxide (GO), which are the most efficient absorbents among others for phenol removal, and then, nanocomposites Titanium dioxide (TiO$_2$)/SBA-15 and TiO$_2$/GO were synthesized. Then, the structural and physical properties of nanocomposites were identified through X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET), Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) analysis. Considering the results of the Response Surface Method (RSM) for phenol removal in the initial study, nanocomposites TiO$_2$/SBA-15 and TiO$_2$/GO were used to remove the same amount of phenol from aqueous solutions.

KEYWORDS: Phenol; Heterogeneous Photocatalytic process; TiO$_2$/SBA-15 Nanocomposite; TiO$_2$/GO Nanocomposite; Response Surface Methodology.

INTRODUCTION
Among the Advanced Oxidation Processes (AOP), Heterogeneous Photocatalyst has proven its efficiency destroying a wide range of organic contaminants to CO$_2$, water and biodegradable mineral acids. In addition,
Heterogeneous Photocatalysis is not limited to water purification, but also used in air purification and treatment, amongst other processes. This process, operating in conditions of temperature and environment pressure, has the ability to remove several species of contaminants in aquatic and gas environments and therefore has the relative superiority over other methods [2].

TiO$_2$-based photocatalysts with a large special surface area and porosity that lead to surface absorption of aquatic contaminants should be built in line with promotion of AOP in practical applications. One of the common strategies is applying TiO$_2$ in periodic mesoporous supporting materials such as Silicon dioxide (SiO$_2$). These materials have a wide surface area, adjustable pore size and a high volume of pores that facilitate release of TiO$_2$ and absorption of pollutant molecules. In recent years, TiO$_2$ is associated with high-grade mesoporous silica materials such as SBA-15, MCM-41 and MCM-48. These periodic mesoporous silica supporters encompass a wide surface area and a high-level range of mesoporous with holes that are designed in a way to permanently support the TiO$_2$ species being resided in. In addition, the large surface area of mesoporous SiO$_2$ has led to the entire release of the TiO$_2$ species. GO can also be a good supporter for Nano-composite materials due to its sheeted structure and highly specific surface. Due to these advantages, periodic mesoporous materials containing TiO$_2$ are more efficient in photocatalytic degradation of waste water in comparison to unsupported TiO$_2$ [1].

In this study, Nano-composites TiO$_2$/SBA-15 and TiO$_2$/GO were prepared as the most efficient Nano-composites amongst the other absorbents for the removal of phenol out of water. Nano-composite TiO$_2$/SBA-15 was prepared by sol-gel method with a two-dimensional hexagonal structure in an acidic environment using mesoporous silica. TiO$_2$/GO was synthesized by thermal hydrolysis. Synthesized samples were analyzed by various methods, such as Xrd, FESEM, TEM and BET. Experimental design of RSM was applied to achieve optimal amount of parameters affecting photocatalytic process of phenol removal. Comparison of phenol adsorption was done by Nano-composites TiO$_2$/SBA-15 and TiO$_2$/GO.

**EXPERIMENTAL SECTION**

**Specifications of applied materials:**

TiO$_2$ (Degussa P25): {Specifications: white, size 21nm, surface area 65m$^2$/gr}

P123, Tetraisopropyl orthotitanate (98%), Tetraethyl orthosilicate (99%), Ethylene glycol (99%), Hydrogen peroxide (33%), Kaliumdihydrogenphosphate (Merck), Nitric acid (65% Merck), 1-phenyl-2,3-dimethyl-4-aminopyrazolon-(5)(Merck), Kaliumhexacyanoferrat (III) (Merck), Dikaliumhydrogenphosphat (Merck), Phenol (99% Merck).

**Synthesis of SBA-15**

The copolymer P123 was firstly stirred into deionized water for 3 hours, and then 2 M Hydrochloric acid was added to that. The mixture was stirred for 2 hours at a temperature of 40°C, then Tetraethyl orthosilicate (TEOS) was added. In the end, the product was stirred for 24 hours at 40 °C and then transferred to the reactor temperature at 150 °C and remained there for 48 hours. The filtered product and the white residue was washed 2 to 3 times with deionized water and then the product was calcined for 24 hours at a temperature of 540 °C [18].

**Synthesis of TiO$_2$/SBA-15 Nanocomposite**

First, Titanium Isopropoxide (TTIP) was added to the 1 Molar of Nitric acid solution with a (weight ratio of SiO$_2$/TiO$_2$= 2) and stirred for 2.5 hours. Then, colloidal solution was diluted with deionized water and the pH was reached 3 with 1 M NaOH. With this pH, Electrostatic reaction occurs between positively charged TiO$_2$ and negatively charged SiO$_2$ particles. Then mesoporous silica was added and the mixture was stirred for 2 hours. The materials obtained by filtering, washing and drying were isolated at the temperature of 550 °C for 3 hours with a heating rate 5% [8].

**Synthesis of GO**

In order to make Graphene out of Graphite oxide using the Hummers method, Graphite powder was added to a solution of concentrated Sulfuric acid, Potassium persulfate ($K_2S_2O_8$) and Phosphorus pentoxide and then the reaction mixture was rest in the Ultrasonic bath for 4.30 h at 80 °C. After completion of the above mentioned time, the reaction mixture was cooled at room temperature, and diluted with distilled water. The product obtained was filtered and washed with distilled water. The obtained solid substance was the pre-oxidized Graphite sample. In order for further oxidation, the Graphite sample was added to concentrated Sulfuric acid, at a temperature of 0°C. Then

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Potassium permanganate was gradually added to the reaction mixture and stirred; the reaction mixture temperature was kept constant below 20 °C. After this process, the reaction mixture was stirred for 2 hours at 35 °C and then diluted with distilled water. Adding distilled water to concentrated sulfuric acid generated some heat and in order to maintain the temperature, the reaction mixture was kept in an ice bath to prevent its temperature increasing beyond 20 °C. After that, the reaction mixture was stirred for 2 hours and then distilled water was added. Finally, 30% Hydrogen peroxide was added which changes the color of the mixture to light yellow. The reaction mixture was filtered and rinsed with distilled water and Sulfuric acid to remove extra ions and the resulting solid was dried at ambient temperature [9].

**Synthesis of TiO$_2$/GO**

GO was added to distilled water and the solution was kept in Sonicator for 1 hour to obtain GO sheets. In Nitric acid was mixed with Ethylene glycol. Then Titanium Isopropoxide (TTIP) was added and stirred to be well mixed resulting an orange solution. reaction mixture and GO were put in an ice bath at 5 °C and Tetraisopropyl orthotitanate (TTIP) was added drop by drop to the solution of GO and finally put in the oven at 180 °C for 8 h. The gray-black residue was put in a centrifuge machine for 30 minutes with 5000 rpm and washed several times by Ethanol to remove the extra Ethylene glycol, non-reacted chemical substances and additional irregular TiO$_2$ particles. The product was finally dried in an oven at 60 °C [15].

**Adsorption studies**

GO and SBA-15 are used in this study, which are more efficient in the removal of phenol compared to absorbents Carbon NanoTube (CNT) and Graphene, according to surveys and experiments conducted. The mentioned absorbents are put into Titanium oxide and used in photocatalytic process to optimize the results and increase the levels of TiO$_2$. It should be noted that, the amount of nanocomposites are made equivalent according to the proportion of absorbents used in the synthesis of nanocomposites based on the optimal amount of 0/1 g/L and given that in nanocomposite TiO$_2$/ SBA-15, SiO$_2$ = 2TiO$_2$ and in nanocomposite TiO$_2$/GO, GO/ TiO$_2$ = 3/7. The amount of nanocomposites are calculated as: TiO$_2$/ SBA-15 = 0/3 and TiO$_2$/GO= 0/14.

As you can see in the Fig. 7, during 2 phases of RSM, determining the optimal amount of parameters affecting photocatalytic removal of phenol out of aqueous solution, these results are determined: pH = 6/6, TiO$_2$ = 0/1g/L. Regarding these results, nanocomposites TiO$_2$/SBA-15 and TiO$_2$/GO are used for removal of phenol out of aqueous solutions with concentration 100mg/L, within 420 minutes, UV radiation 250 watts, in a reactor with Pyrex glass cover and slurry bed. The results were analyzed by TOC (Dohrmann DC-190) and the kinetic investigation of absorption reactions were done by the standard photometry methods using UV-Vis spectrophotometer at a wavelength 500nm.

**Characterization**

In order to determine the crystal structure of the absorbent and synthesized nanocomposite, Xrd analysis is prepared by machine Philips pw1729 x-ray generator. Shape and morphology of absorbents are studied using FESEM, Sigma model, manufacturer Zeiss Germany and TEM, KV100C-10EM, manufacturer Zeiss Germany. The pore size, pore volume and surface area of the absorbents are studied through analysis of specific surface BET based on the gas absorbed on the absorbent surface holes, by device Tri-Star II 3020 V1/03, Micromeritic Company of America.

**RESULTS AND DISCUSSION**

**Characterization of SBA-15 and its nanocomposites**

Photocatalytic compounds with nano metric scale, due to the high surface-to-volume ratio, act more efficiently and can break apart colorful substances and organic pollutants in water by generating electron-holes. Researches have shown that regular nano-structured solids like mesoporous silica structures such as the SBA, MCM and HMS, are of special importance in photocatalytic processes compared to amorphous solids and this could be due to reasons such as regular and uniform distribution of holes in surface of the substrate or controllable monotonic density of Catalytically active centers on the surface and the SBAs are significantly superior to MCMs due to easy formation and high stability of these compounds. SBA-15 is an important mesoporous, which is applied as Structural control agent using tri-Copolymer; and because of the relatively large pore size (>6nm) and thick walls of the pores, is used as a guard for the distribution of TiO$_2$, Fig.1
Figure 7: Surface Response diagrams of TiO$_2$, pH and H$_2$O$_2$ parameters affecting efficiency of phenol removal and determining the optimum parameters volume.

Fig. 1: Low angle Xrd diagram of SBA-15 absorbent used in this work.

shows an image of absorbent low Xrd angle SBA-15. The strongest peak, at 2θ=1/01, is seen on Xrd from crystal display 100, indicating the mesoporous structure. The presence of two other low-intensity peak at 2θ=1/65 and 2θ=1/85 is related to crystal Xrd of crystal displays (110) and (200) respectively. These three peaks represent the two-dimensional hexagonal mesoporous structure of SBA-15. After preparation of nanocomposite TiO$_2$/SBA-15, the crystal structure was kept and only the peaks intensity decreased due to the partial filling of cavities. Fig. 2C shows the Xrd image of nanocomposite TiO$_2$/SBA-15. In the range of 2θ=29/7 to 2θ=51/92, 3 distinct Peaks can be seen, which are related to diffraction (100), (110) and (200) indicating the hexagonal structure of mesoporous materials SBA-15 (P6mm). The preparation of nanocomposite TiO$_2$/SBA-15 was therefore successfully done and also the crystal structure of mesoporous was preserved [12]. The Fig. 2,d shows Xrd of commercial TiO$_2$ P25. 3 peaks identified in 2θ=29/11 and 2θ=33/26 and 2θ=43/93 are related to phases of anatase and rutile [7]. Also, as shown in Table 1, pore size and pore volume of nanocomposite TiO$_2$/SBA-15 is high due to its mesoporous structure. The TiO$_2$ crystal size in nanocomposite TiO$_2$/SBA-15 is also decreased as a result of synthesis process.

Characterization of GO and its nanocomposites

GO would easily get layered and distributed in water; the publication is mainly in the form of single-layer plates. Using GO as a practical matter at the nanoscale to create nanocomposites along with metal oxides has been extensively studied. The reason is to achieve a kind of hybrid that has met features of both GO, namely its paper mode, and also features of metal oxide nanoparticles.

GO function in Nanocomposites is as bellow:

a) GO sheets provide good conditions for the deposition of TiO$_2$ nanoparticles

b) These sheets can upgrade absorption ability of TiO$_2$/GO nanocomposites

c) GO acts as electron receiver and photo sensitizer and effectively increases photo analysis of Butane [14].

Fig. 2,b is related to Xrd of the nanocomposite TiO$_2$/GO. TiO$_2$ crystals in the middle of the image contain a mixture of anatase and rutile. Peaks (101), (004), (200), specified with a circle, indicate anatase phase and other peaks (110), (101), (111), (211), specified with a diamond, indicate rutile phase. Further, in Fig. 2,a there is a very

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Table 1: Studying the specific surface area, pore size, pore volume and the size of crystalline TiO$_2$ nanocomposites in nanocomposites TiO$_2$/GO and TiO$_2$/SBA-15.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore size(nm)</th>
<th>TiO$_2$ crystal size(nm)</th>
<th>BET (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/P25</td>
<td>0/122003</td>
<td>0/0021</td>
<td>28/2</td>
<td>50/6045</td>
</tr>
<tr>
<td>TiO$_2$/GO</td>
<td>0/246156</td>
<td>4/65</td>
<td>6/6</td>
<td>211/3995</td>
</tr>
<tr>
<td>TiO$_2$/SBA-15</td>
<td>0/606071</td>
<td>11/93</td>
<td>7/3</td>
<td>203/0484</td>
</tr>
</tbody>
</table>

Fig. 2: Wide-angle Xrd diagram of adsorbents and nanocomposites used in this work.

The peak 2$\theta$=14/62 (002), which is related to GO crystal. The peak 2$\theta$=14/62 in Nanocomposite TiO$_2$/GO has extremely decreased compared to the peak (002) GO on the Figure a, and XRD peak GO (100) on 2$\theta$=49/75 has completely disappeared. Results show that the GO has more widely got laminated to form GO, [Tio]$^{2+}$ groups in the solution are absorbed on the surface of GO, and then growing crystals of TiO$_2$ on the layered structure of GO is formed and finally Nanocomposite TiO$_2$/GO has formed [11].

TiO$_2$ P25 BET is 50/6045 m$^2$/g, which is higher than other types of commercial TiO$_2$ [7]. According to the classification International Union of Pure and Applied Chemistry (IUPAC), Micro and Macro pore materials have respectively diameters less than 2nm and more than 50nm, and therefore mesopore materials are placed between them. Therefore, the pore size of all samples is in accordance with the classification of (IUPAC), type IV, and related to the porous structures with pore sizes between 2 to 30 nm.

In nanocomposite TiO$_2$/GO, GO sheets are coated by TiO$_2$ particles. Therefore, when the surface area of nanocomposite TiO$_2$/GO is measured, mainly it is done according to properties of anatase nanoparticles. For this reason, a relatively low specific surface area of nanocomposite TiO$_2$/GO (211/3995 m$^2$/g) is observed compared to the theoretical value of Graphene and GO. The total surface area of nanocomposite TiO$_2$/GO (211/3995 m$^2$/g) is higher than the nanocomposite TiO$_2$/SBA-15 that could be caused by the layered morphology of GO.
Morphology

Information about materials appearance can be achieved through analysis of FESEM and TEM. To determine the order of pores in the oxide materials mixture, the difference between their sizes and appearances, the best image analysis is FESEM, which is even better than TEM analysis [12].

**TiO$_2$/SBA-15**

FESEM image of nanocomposite TiO$_2$/SBA-15 in the Fig. 3, shows the string-shaped morphology of the nanocomposite that contains a number of threads size 1-2µm that are so dense to become like a mass. These images show that after combination of TiO$_2$ with SBA-15, SBA-15 keeps its primary string-shaped morphology indicating its high stability and good protection for TiO$_2$ particles. The appearance of nanocomposites prepared is totally in accordance with the results of previous authentic studies [19]. TEM image of nanocomposite TiO$_2$/ SBA-15 in the Fig. 4, indicates quite regular hexagonal array of two-dimensional mesoporous channels that proves the nanocomposite has a hexagonal structure P6mm, which is specification of SBA-15. Pipe-like channels of the holes of nanocomposite TiO$_2$/ SBA-15, is one of the most important structural features of this nanocomposite for optimal photocatalytic activity. This is due to the branched channeled frame which facilitates access to activate reaction sites on the frame of the wall [8].

SBA-15 absorbent has also some optimal surface and physicochemical characteristics such as low toxicity, biocompatibility, biodegradability and synthesis using cheap resources, and therefore, its use in this study adds to its importance in addition to its high efficiency in the removal of phenol.

**TiO$_2$/GO**

Fig. 5, shows the FESEM image of TiO$_2$/GO. In this image we can see a lot of TiO$_2$ nanoparticles well located among GO sheets in an area of about 200 nm which represent a good synthesis of nanocomposite TiO$_2$/GO. Fig.6 shows the TEM image of TiO$_2$/GO. Diffraction spots in nanocomposite TiO$_2$/GO, relate to the various crystal displays of the tetrahedral structure of the crystal TiO$_2$ cells like (101), (004) crystals of anatase, and rutile crystals (301). However, the diffraction spots of the crystal displays (100) are for hexagonal structure of crystal cells.
of GO, and diffraction spots scattered below the hexagonal lattice relate to the crystal (101) of crystalline cells of TiO$_2$ tetragonal structure. The results show the presence of TiO$_2$ particles below GO sheets, although the number of TiO$_2$ particles is relatively low. TEM analysis confirms accumulation and growth of TiO$_2$ particles among and out of GO sheets, which is in accordance with FESEM analysis [11].

COMPARATIVE STUDIES ON AOPs

To reduce the problem of water scarcity, water needs to be purified and reused. Contaminated water purification process is based on mechanical, biological, physical and chemical firms. After filtration and removal of suspended particles (Primary treatment), biological treatment is appropriate (Secondary treatment). Unfortunately, there are such products as non-biodegradable for which, more effective methods than non-reactive systems are required such as volatility, absorption on granular activated carbon, burning, ozone and oxidation (Advanced treatment). The aim of these processes is water treatment, and thus improves water quality but some of these technologies, (such as filtration and absorption) just concentrate contaminants transferring them from one phase to another [2]. Various methods are applied for water treatment and sewages containing organic materials such as phenol. Methods such as using TiO$_2$ coated on activated carbon, in which, the combination of TiO$_2$/AC would be consumed over time by photocatalytic reaction and its efficiency would be gradually reduced. Also using Homogeneous Fenton Processes after which, large amounts of ferric salt (containing iron compounds) should be collected. In addition, the technical tools needed to optimize or monitoring the efficiency of the Fenton reaction, are complex and expensive, so their use is not common. using carbon nanotubes to remove phenols from water that requires too much energy and carbon nanotubes quickly spread in the environment and are toxic to humans and the environment, as well as the removal of phenol out of water by TiO$_2$ coating on the tube glass that has lower efficiency compared to nanocomposites used in the present study. Therefore, considering the problems of mentioned methods, efficiency of heterogeneous photocatalytic process and nanocomposites used in this study is more visible.

Based on the results, as can be seen in Table 2, both nanocomposites which have been used in this work, have
high potential in the removal of phenol out of aqueous solutions. The results were analyzed using the spectrophotometer UV-Vis at a wavelength of 500nm. Therefore, The photocatalytic process is very effective in the removal of phenol from aqueous solutions. However, the effectiveness of the process seriously depends on test conditions. The catalyst, The time of UV radiation, pH, and Light intensity were important parameters in the destruction process. Studies also show that TiO\textsubscript{2} (Degussa P25) is very active in the destruction of phenol and phenol degradation is very effective at a neutral pH.

**CONCLUSIONS**

This research was conducted to evaluate different absorbents and determining nanocomposites suitable for the removal of phenol out of aqueous solutions with high efficiency. The reader of this article will get a good image of different ways to remove phenol out of water and the main goal of each procedure. The heterogeneous photocatalytic procedure was used in the removal of organic contaminants due to its high efficiency. In this study, the nanocomposites TiO\textsubscript{2}/GO and TiO\textsubscript{2}/SBA-15 were used for the removal of phenol out of aqueous solutions. Furthermore, this study briefly highlights the procedure for nanocomposite synthesis.

- The experimental results indicate that, the synthesized nanocomposites show more efficiency compared to the net TiO\textsubscript{2}. In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology to align with the “zero” waste scheme in the water/wastewater industry. The ability of this Advanced Oxidation Technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water [2].

- It is generally believed that the efficacy of AOPs to treat a certain waste stream is a strong function of (i) the composition and concentration load of the stream in question and (ii) the treatment aim itself. In fact, the higher the polluting load and the extent of pollution removal needed, the more harsh the treatment conditions to be applied are. So, treatment performance can be enhanced through coupling various processes for example,(a) Simultaneous application of different AOPs to promote the rate of organics oxidation,(b) Sequential application of various AOPs to enhance selectivity,(c) Application of a separation treatment prior to AOP treatment to transfer pollutants from the liquid to another phase so that they can be treated more easily and
do not intervene with advanced oxidation.(d) Application of AOPs as a pre-treatment stage to enhance biodegradability and reduce toxicity, followed by biological post-treatment. (e) Complex treatments comprising various physical, advanced oxidation and biological processes. Optimal treatment schemes will eventually be decided upon achieving discharge limits set by national or international environmental regulations at a reasonable cost. This, in turn, will be dictated by the type of waste stream to be treated, i.e. its composition, concentration, biodegradability and toxicity [3].

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