Article

Synthesis and characterization of binaryTiO_2/AC nanocomposite for photocatalytic degradation for organic Congo Red dye removal

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Abstract

The synthesis, characterisation, and photocatalytic activity of titanium dioxide nanoparticles (ADT) doped with activated carbon and supported on environmentally activated carbon (PAC) have been covered in this work. Under visible light (496 nm), the photocatalytic activity of the nanocomposite was examined for the degradation of Congo Rd (CR) dye from aqueous solution. It was found that, for a 25 ppm CR solution, 100% degradation occurred in 90 minutes.This study used a UV-visible spectrometer to explore the photocatalytic degradation of Congo Red dye by TiO_2/AC under UV irradiation. The obtained samples were characterized by X-ray diffraction (XRD), Field Emission-Scanning electron microscopy (FE-SEM), and Energy Dispersive X-ray dispersive spectroscopy (EDX). It also demonstrated that the Congo Red dye photocatalytic degradation reaction was fitted to a pseudo-first-order reaction. Findings indicated that Congo Red Dye (CRD) treatment.

Keywords:ADT,PAC,TiO_2/AC, CRD, photocatalyst and nanocomposite.

1.Introduction:

In recent years, there has been a growing awareness of the pollution that increased industrialization causes to wastewater. A complex mixture of heavy metals, organic compounds, and azo-dyes are present in industrial wastewater discharged primarily from the paper and textile sectors. These pollutants are difficult to remove from natural habitats because of their high solubility, stability, and limited biodegradability in aqueous conditions.

Azo-dyes are poisonous, obstruct light flow, and hinder the growth of aquatic plants and animals. Furthermore, since the azo group (N=N) is transformed into aromatic amines, which have the potential to cause cancer in people, some dyes and the intermediates that result from their breakdown may also be regarded as potential pollutants. Thus, it could result in major environmental issues and have an immediate impact on aquatic ecological systems and human health if these wastes are dumped into receiving sources (such as rivers and creeks) without first being treated [1,2]. The term "activated carbon" (AC) describes highly carbonaceous materials made from coal, wood, coconut shells, cones, and other materials with high porosity and sorption ability.

One of the adsorbents that is commonly employed in many sectors to remove a variety of contaminants from air and water bodies is AC. Since AC is made from agricultural and waste materials, it has shown to be a fantastic substitute for the more conventionally utilized costly and nonrenewable sources [3].The n-type semiconductor titanium dioxide (TiO_2) finds extensive application as a photocatalyst because of its favorable thermal stability, inexpensive cost, non-toxic nature, and environmental friendliness. Numerous rocks and sands naturally contain titanium dioxide.

TiO_2 is a semiconductor material with a band gap of 3.2 eV that can be triggered by light.TiO_2, one of the most popular photocatalysts, is utilized so extensively because of its beneficial properties, which include high photocatalytic activity, chemical stability, affordability, and availability. TiO_2 is found in crystal

forms such as rutile and anatase. Its unique surface characteristics and band-gaps greatly affect its photocatalytic activity and selectivity. Most people agree that anatase TiO_2 is the most active of these forms [4,5]. Because photocatalysis can be done under ambient circumstances and can use atmospheric oxygen as the oxidant, it is gaining more attention. Additionally, the method makes use of widely accessible, reasonably priced, nontoxic semiconductor catalysts like TiO_2 and ZnO, which completely mineralize organic compounds into CO_2, water, and mineral acids [6]. A number of photocatalysts, including ZnO, SnO_2, and TiO_2, were only useful in ultraviolet (UV) light, which accounts for less than 5% of solar radiation. As a result, a large number of materials with narrow band-gaps were created extensively for the removal of pollutants by photocatalysis [7]. One of the most thorough and economical methods of purifying water that makes use of semiconductor materials and renewable resources is photocatalytic treatment. Because semiconductor-based photocatalytic systems require less chemical elements than other Advanced Oxidation systems (AOPs), they are more commonly employed. Unlike other AOPs that use expensive oxidants like H_2O_2 and O_3, it also uses natural oxygen as an oxidant. Recently, there has been a lot of interest in heterogeneous photo catalysis using oxide semiconductors because of its potential applications in organic synthesis and environmental applications [8]. Figure (1).

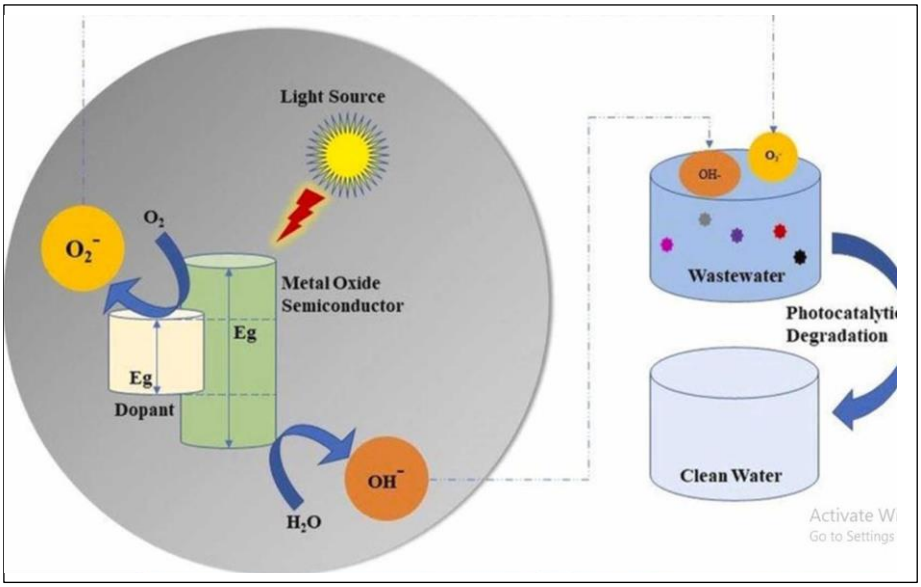


Figure (1): Diagram schematic for photocatalyst photoactivation[8].

The dyes are organic compounds that are soluble; they specifically belong to the groups of bases, acids, reactive, and directed. The capacity to fix color in a material is attributed to auxotrophic groups, which are polar and can bind to polar groups of textile fibers; however, this characteristic is not present in all materials [9].Different types of dyes are categorized according to their intended use: basic, acidic, mordant, direct, reactive, vat, dispersion, sulfur, and azotic [10].

The dye industry has expanded dramatically in recent years. Commodity dye production is estimated to be in the tens of thousands according to the US "Color Index". About 60,000 tons of color-containing trash are released into the environment annually, with azo dyes accounting for 80% of this total [11]. X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM) with energy dispersive X-ray dispersive spectroscopy (EDX), and visible irradiation technique were used to evaluate the photodegradation of Congo red solution. TiO_2/AC nanocomposites were characterized using these methods.

2. Materials and method

Every chemical employed in this investigation was extremely pure and didn't require additional purification before usage. Commercial TiO_2powder was procured from Sigma-Aldrich in Germany; Scharlau provided the sodium hydroxide (NaOH, 99%), Congo red dye (C32H22N6Na2O6S2, M.wt= 696.7 g/mol), and activated carbon (99%).

2.1 Preparation of TiO_2 doped AC nanocomposite

The TiO_2/AC NPs were created by dissolving 2 g of commercial TiO_2 in 100 mL of distilled water (DW). The mixture was then slowly added 1 M sodium hydroxide until the pH of the solution reached 8 while being constantly agitated with a magnetic stirrer for 3 hours. After that, a certain quantity of activated carbon (AC) was added to the solution mentioned above, and it was agitated for four hours at 60 °C. Centrifugation was used for 60 minutes at 8000 rpm to separate the resultant precipitate. Following a 4-hour vacuum oven drying process at 75 °C, the precipitate was further calcined in air for 1.5 hours at 350 °C.

2.2 Photo catalytic decomposition experiments

Degradation reactions are carried out to assess the produced catalyst's activity. First, we need to ascertain the impact of catalyst loading. The studies were conducted using various catalyst concentrations for dye solutions and dye concentrations (ppm) at room pH. A 250 ml Pyrex glass beaker and a magnetic stirring apparatus with an oxygen bubble source made up the reactor. Above the beaker, the bulb was positioned perpendicularly. There were 15 centimeters separating the Pyrex glass beaker and the lamp. It was found through analysis using a (UV-Visible) spectrophotometer that a centrifuge was required in order to remove the minor amounts of (TiO_2/AC) that were useful. A (UV-Visible) spectrophotometer [(Type Shimadzu, Japan, PC 1650-303,

University of Karbala/College of Education for Pure Science-Chemistry Department)] was used to measure the dye concentration. 298 K was the temperature utilized in each test.Aldrich's Red dye by Sigma-Congo. The compound known as Congo Red is an organic substance that is the sodium salt of4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2- yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate.

It's an azo dye. Congo red dissolves in water to form a crimson colloidal solution, although it dissolves more readily in organic solvents. Due of Congo red's carcinogenic qualities, the textile industry has long since stopped using it [12]. Since cationic dye models were used to assess photocatalytic performance, TiO_2/AC NPS was distributed in an aqueous dye solution containing 25 ppm. Before the suspension was subjected to radiation, it was magnetically agitated for 90 minutes in the dark to bring the dye's adsorption and desorption processes into balance. Approximately five milliliters of sample were obtained throughout each of the fifteen minutes of testing. The aqueous solution was centrifuged to remove any suspended solid particles. Using distilled water as a reference, the residual dye concentration in a CRD solution contained in a micro-cuvette was measured at 496 nm using a UV-visible spectrophotometer , see figure (2). The degradation efficiency was calculated using the following equation. The degradation efficiency was calculated using the following equation:

$$\textbf{Photo Decomposition Efficiency(PDE) (\%)} = \frac{C0 - Ct}{C0} \; X \; 100 \quad \text{----------(1)}$$

Where C_o: is the dye concentration at the start of the test, and C_t: is the dye concentration following a period of testing (t)

The pseudo-first-order kinetic model was employed to investigate the organic dye's photocatalytic degradation kinetics in the presence of the photocatalysts.

$$\ln(C_0/C_t) = kt \quad \text{----------(2)}$$

where t is the time interval, k is the rate constant, and C0 and Ct are the model dye's concentrations before and after radiation, respectively. The rate constant can be found by sloping the plot of ln(C0/Ct) vs. t, as shown in figures (7) and (8) [2].

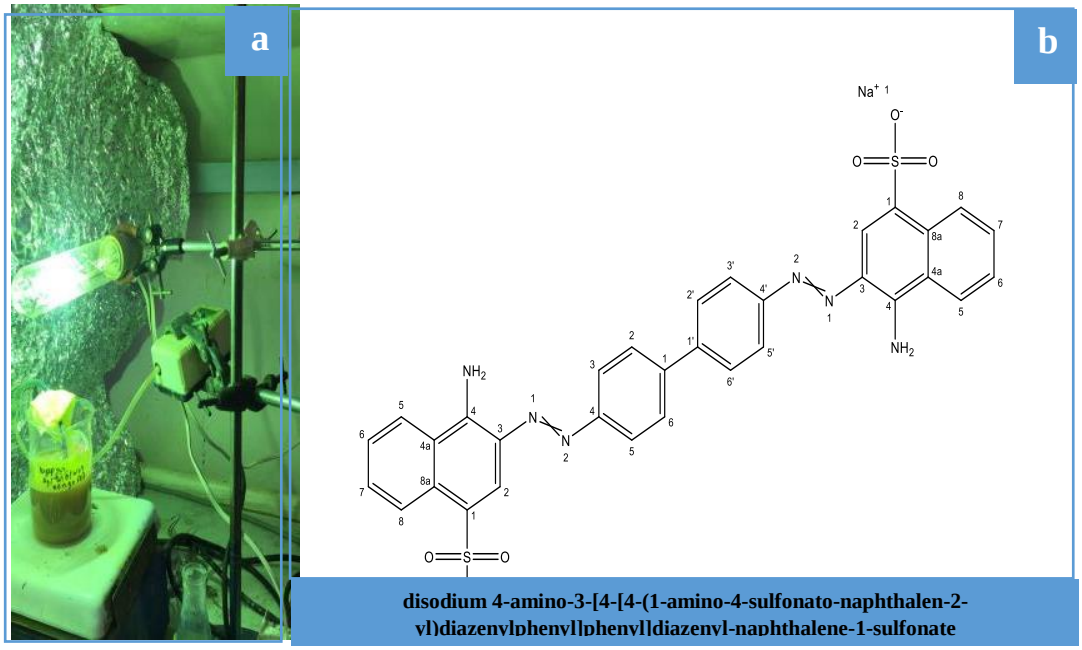


Figure (2): (a) Photo-degradation of real image sample CR dye , and (b)The CR dye molecule's model and structure.

3. Result and discussion

3.1 Characterization of loaded TiO_2 on Activated Carbon nanoparticles

The XRD pattern of TiO_2/AC NPs is shown in figure (3). The diffraction peaks at 28°, 38°, 50°, 55°, 56°, and 64° here were all in good agreement with the anatase phase of TiO_2/AC NPs. No additional summits suggest the existence of impurities due to the influence of calcination (350 C^o). (JCPDS card no. 21-1272) The diffraction peaks seem to have a clear, crisp crystal form. The following method was used to measure the TiO_2/ACnanocomposite's crystallite size: Debye - Scherrer's [13].

$$\textbf{Crystalline size (D)} = \frac{K\lambda}{\beta\cos\theta} \text{ nm}$$

Where λ is the wavelength of the Cu-Kα X-ray (λ = 1.5406 Å), θ is the diffraction angle, and β is the full width at half maximum (in radians). K is the Debye Scherrer constant.

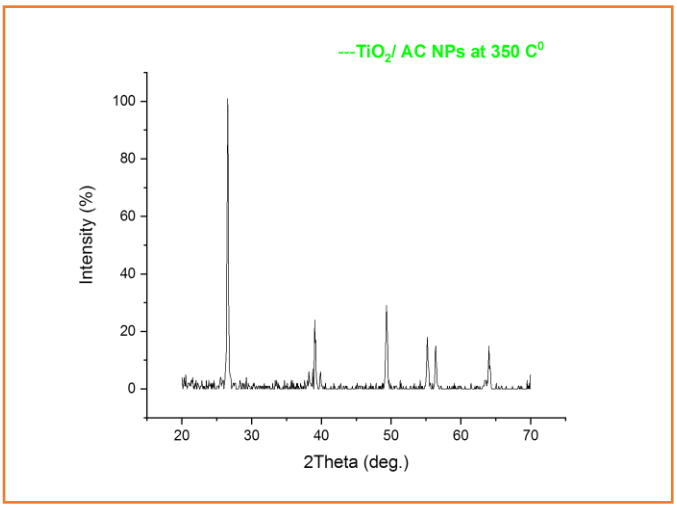


Figure (3): TiO_2/AC nanocomposites XRD spectra.

Using FE-SEM analysis, the produced materials' average size and surface morphology were determined. Figure (4) represents the FE-SEM images of prepared TiO_2/AC nanocomposites. The TiO_2/AC needles have an average size and diameter of 71.52 nm. The movement of photoexcited charge carriers on the surface of TiO_2/AC nanocomposites is caused by the flake, spherical, and one-dimensional (1D) needles that can be seen in the FE-SEM picture of the nanocomposites; In the course of the degradation process, it may suppress the rate of electron-hole pair recombination [14].Using EDX mapping on an EDX microanalysis system, the element distribution of these TiO_2/AC nanocomposites can be found in figure (5). The elements Ti, Na, Mg, Ca, C, Au, O, and Al have signals linked to the Map Micrograph Technique (MMT).

The nanocomposites' EDX spectra are displayed in figure (5).The TiO_2/AC micrograph also shows some agglomerations, which could be caused by mild electrostatic interactions and polar attraction between the particles. Furthermore, since

all of the TiO_2 particles were sintered at a high temperature (350 °C) to guarantee complete crystallization, this behavior may have resulted from particle adhesion. TiO_2/AC NPs showed rough porous architectures and were evenly distributed on the surface of AC, suggesting that the TiO_2/AC nanocomposite was successfully synthesized [15].

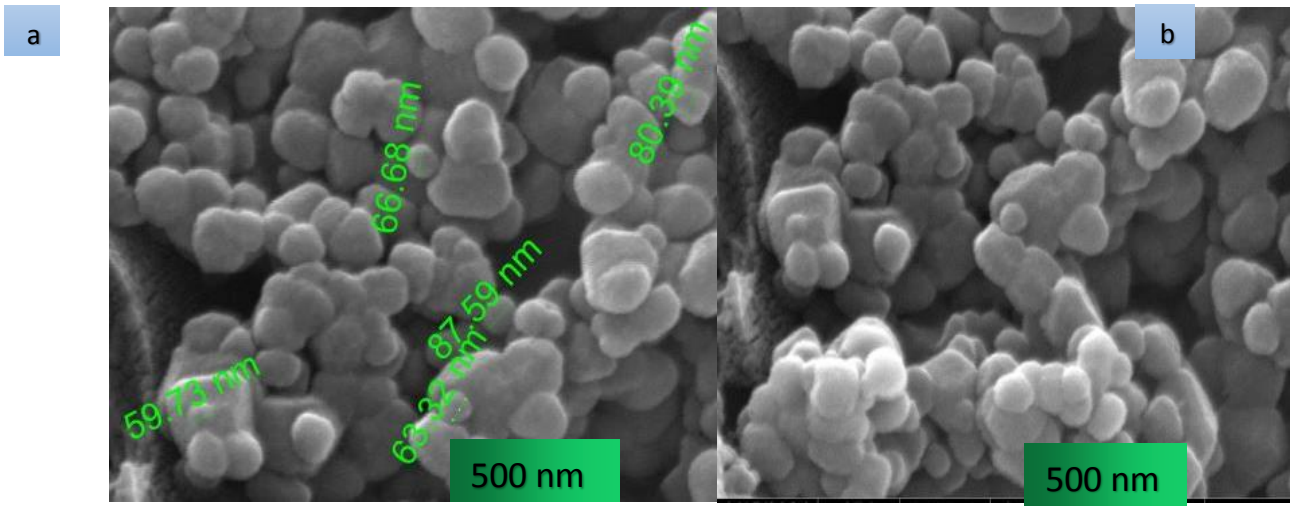


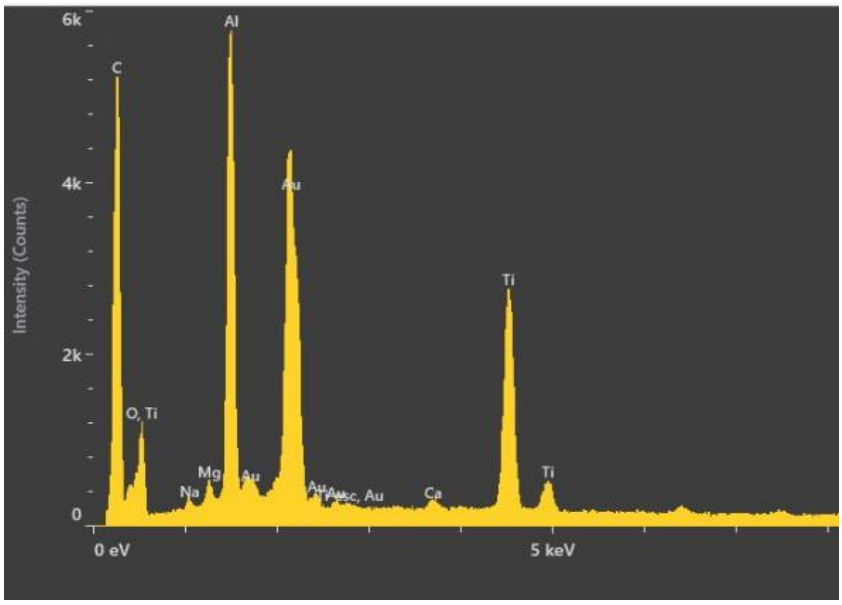
Figure.4: (a) and (b) TiO_2/AC nanocomposite image captured by FE-SEM with particle size and without respectively .

The presence of the TiO_2/AC nanocomposite was confirmed by energy dispersive X-ray dispersive spectroscopy, or EDX. The TiO_2/AC nanocomposite nanocrystal line exhibits strong and precise diffraction peaks,indicating good crystallinities. The EDX spectra of the pure TiO_2/AC nanocomposite reveal the presence of only Ti, C, O, and Al. Table (1) provides a semi-quantitative assessment of the atomic concentration (atom%). It indicates that the products' TiO_2/AC elements content is (3.7,0.3, 0.4,0.2,68.7,3.0,16.2 and 7.5) for Titanium (Ti), Sodium (Na), Magnesium (Mg), Calcium (Ca), Carbon (C), Gold (Au), Oxygen (O), and Aluminum (Al).

Table(1): TiO_2/AC nanocomposites' composition was examined using EDX.

Sample	Ti Atomic %	Na Atomic %	Mg Atomic %	Ca Atomic %	C Atomic %	Au Atomic %	O Atomic %	Al Atomic %
TiO_2/AC NPs	3.7	0.3	0.4	0.2	68.7	3.0	16.2	7.5

The EDX results are shown in figure (5), where it is evident that the weight ratios of TiO_2/AC NPs were, respectively, 59.73 %, 63.32, 66.68, 80.39, and 87.59 %. The EDX examination showed that the sample contained the necessary phases of Ti and O and that the produced TiO_2/AC NPs were highly pure. Similar Ti, O, and AC ratios that are near to the theoretical values are seen in the EDX results from the current investigation.

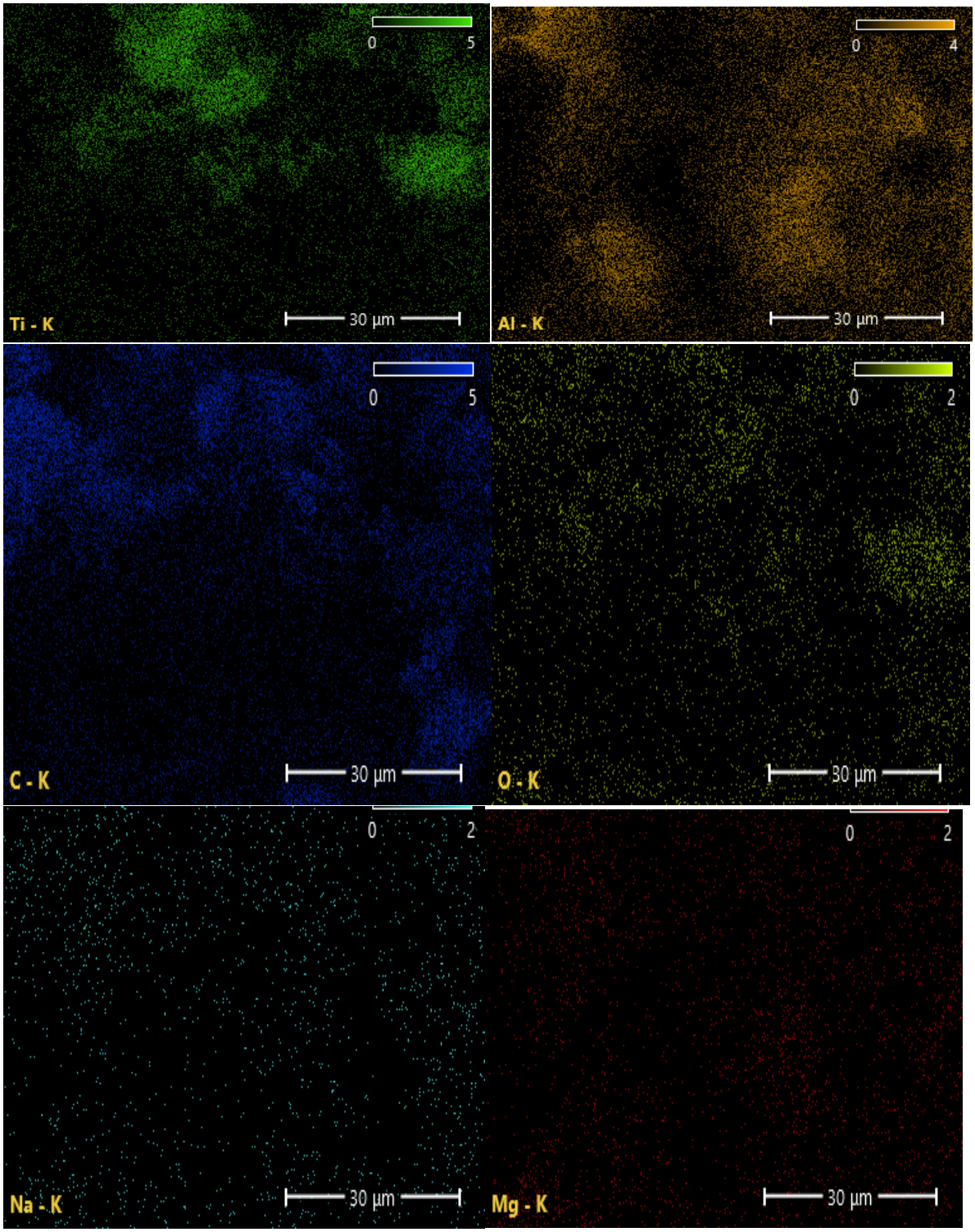


Map sum spectrum of TiO_2/AC NPs

Elemental	Atomic %	Weight%
Ti	3.7	0.1
O	16.2	0.6
C	68,7	0.3
Na	0.3	0.1
Mg	0.4	0.0
Al	7.5	0.1
Ca	0.2	0.0
Au	3.0	0.5

Figure (5): Pure TiO_2/AC NPs elemental mapping and EDX analysis.

TiO_2/AC NPs samples' chemical composition is revealed by EDX analysis. The produced samples are mostly made up of Ti, O, C, Na, Mg, Al, Ca, and Au, with very little Ca and Mg present, as shown in figure (6).


0
5
Ti - K
30 µm
0
4
Al - K
30 µm
0
5
C - K
30 µm
0
2
O - K
30 µm
0
2
Na - K
30 µm
0
2
Mg - K
30 µm

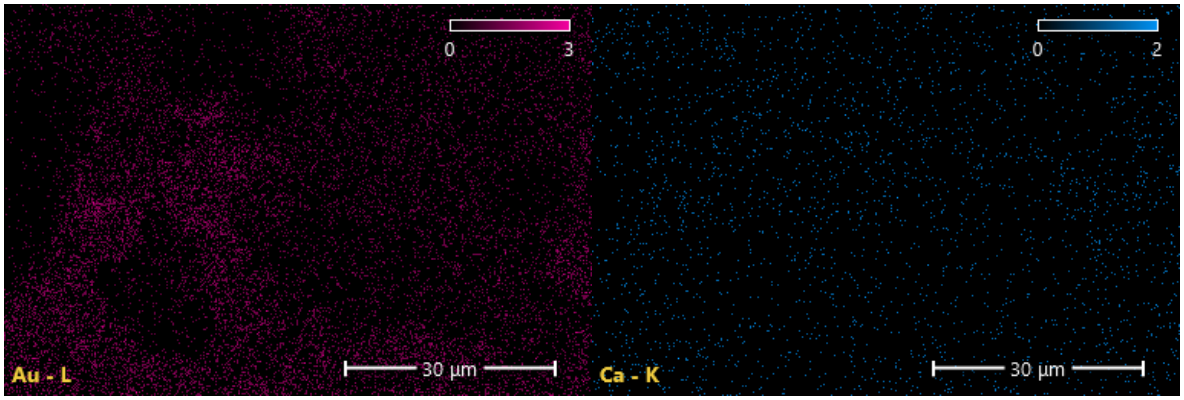


Figure (6): EDX analysis of TiO_2/AC NPs

3.2 Influence of various TiO_2/AC nanocomposites photodeposition process parameters on C R dye.

3.2.1 Effect of mass dosage

Impacts of a photocatalyst concentration of (0.2.0.4.0.6.0.8) gram on the (CR) dye photocatalytic degradation at reaction temperatures of 25 °C for 1.5 hours. It is possible to assess the experimental results under the assumption, as shown in figure 7(a) and (b). A pesudo first order kinetic model was used to discuss the findings [16]. The impact of catalyst surface mass (TiO_2/AC) nanocomposites on the dye photodegradation process is depicted in figure (7). Various weights (0.2, 0.4, 0.6, and 0.8) gm per 100 ml of dye solution were used in the study.

Due to this factor, all settings must stabilize (25) ppm for dye concentration and 1.71 mW/cm2 for light intensity. Congo Red Dye After that, the catalyst surface (TiO_2/AC) nanocomposite and red dye solution were combined, and the mixture was stirred for 90 minutes under UVA light (using a UVA LED lamp). Following that, the supernatant was separated by centrifugation at 150 rpm, and the concentration that remained was determined using a UV-visible spectrophotometer set to 496 nm in wavelength.

When (TiO_2/AC) NPs are added in an increment of 0.2 gm to 0.8 gm, the photocatalytic efficiency increases from 50% to 97% in 1.5 hours. The number of active sites on the catalyst surface increased due to an increase in mass, and this in turn accelerated the pace at which radicals develop [17]. The catalyst weight of 0.2 gm produced the largest decrease in the C/C^o value, as shown in Figure (7-a). In contrast, figure 7-b shows that when the photocatalyst dose was increased from 0.2 to 0.8 gm, respectively, the PDE% values grew consistently 97%. Overall, the higher CR PDE% was achieved with 0.8 gram of TiO_2/AC photocatalyst. The presence of more active sites on the photocatalyst surface may affect the photocatalytic performance.

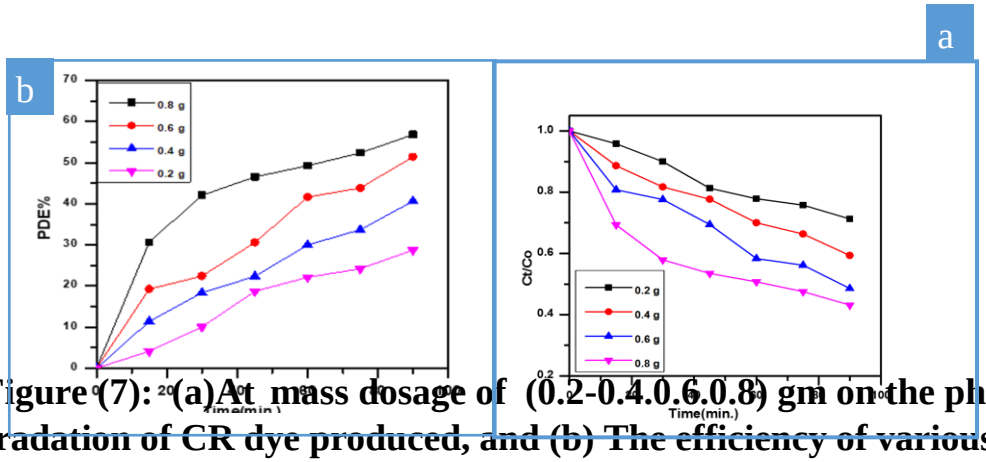


Figure (7): (a)At mass dosage of (0.2-0.4.0.6.0.8) gm on the photocatalytic degradation of CR dye produced, and (b) The efficiency of various mass dosages on the photocatalytic degradation of CR dye.

3.2.2 Effect of CR dye concentration

Different CR(25-100) ppm concentrations were used in order to examine the effect of the dye's starting concentration upon TiO_2/AC. A bulk dosage of 0.4 gm is displayed in figure (8). The main ingredient of the dye solution has a big impact on how quickly CR degrades. The dye's photocatalytic degradation in relation to concentration and duration [18]. The experimental data could be assessed under the assumption of pseudo first order kinetics, as shown in figure (8-a).To assess the use of the TiO_2/AC nanocomposite surface as a catalyst for the textile pollution-causing dye Congo Red's photodegradation. To examine how the initial concentration of Congo Red dye affected the efficiency of TiO_2/AC NPs, a number of dye concentrations ranging from 25 to 100 ppm were carefully selected. Investigated the room

temperature photocatalytic breakdown rate of (CR) dye. For 1.5 hours, the light intensity was 1.71 mW/cm2 and the amount of TiO_2/AC was 0.8 gm. See figure (8-b). Because there are fewer photoactive sites available for the sorption of OH– ions required to produce OH radicals, an increase in the initial dye concentration results in the loading of more dye molecules on the photocatalyst surface, which inhibits the formation of OH species.

Therefore, for a given reaction temperature, photocatalyst dose, and illumination period, the production of OH radicals on the photocatalyst surface remains constant due to the unavailability of active sites [19]. At high concentrations (25 and 50 ppm), the OH species that are generated are therefore inadequate for the photocatalytic destruction of CR dye. Additionally, because of the potential for dye molecule aggregations at high concentrations, PDE% may be impacted by limitations on light penetration and/or absorption. These findings demonstrate that the photocatalytic degradation of CR dyes adheres to a pseudo first order kinetic model[20].

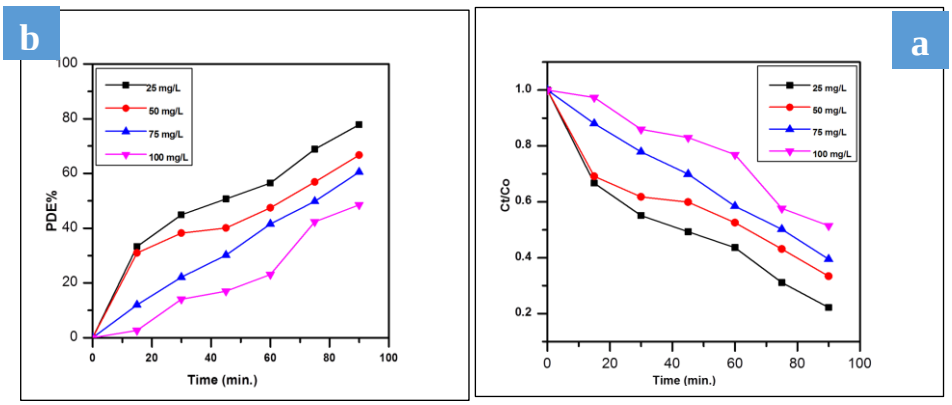


Figure (8): (a) The effect of TiO_2/AC NPs at concentrations of 25–50–75–100 ppm on the photocatalytic degradation of CR dye generated; and (b) the effectiveness of CR dye concentration.

4. Conclusions

The photocatalyst of TiO_2 activated carbon composite (TiO_2/AC) used in this study was made economically and at a reasonable cost using the precipitated

technique.as well as other related factors like effect mass dose and concentration. According to the catalyst's characterization, TiO_2 was evenly distributed across the surface of the activated carbon. The XRD, FESEM, and EDX methods verified the effective synthesis of nanomaterials. According to the results of photocatalysis degradation for CR, the TiO_2/AC nanocomposite exhibited higher activity (PDE%= 97). The photocatalytic degradation reaction adheres to the pseudo first order paradigm, as demonstrated by the kinetic analysis. The produced composite material is therefore very useful for the treatment of wastewater from the environment and the elimination of dyes.

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