Synthesis and Photocatlytic Application of Drinking Water Treatment Sludge @ TiO₂ Composite for Degradation of Methylene Blue Dye

Rashed, M. N.[1*], El Taher, M. A.[1] and Fadlalla, S. M. M.[2]

1. Chemistry Department, Faculty of Science, Aswan University, 81528 Aswan, Egypt

2. Aswan Company for Water and Wastewater, Aswan, Egypt

ABSTRACT: Sludge/TiO₂ composite was synthesized from drinking water treatment sludge, as a waste material and TiO₂ , by a sol- gel method. Various sludge adsorbent / TiO₂ ratios (1:1, 1:2 and 2:1 w/w) were prepared, and characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray Fluorescence (XRF), and BET. The prepared composites were applied successfully for photodegradation of methylene blue (MB) dye from a solution. The photocatalytic degradation of MB dye was investigated using UV irradiation, or UV/H₂O₂. Initial dye concentration, solution pH, composite dosage, and UV irradiation time were applied to study the optimum conditions for MB degradation. The results revealed the highest MB dye degradation with composite (2:1). It was found that the maximum MB degradation efficiency was at pH=7, 4 h irradiation time, 0.125 g composite dose, and 50 ppm initial dye concentration. MB removal efficiency was 95.7% using UV irradiation, and 99.8% of that using UV/ H₂O₂. The rate of MB dye degradation followed the first order kinetics. Results from this study offer the best conditions for recycling drinking water treatment sludge, and use it for wastewater treatment.

Keywords: methylene blue, water treatment, sludge, composite, photocatalysis.

INTRODUCTION

Dyes are pollutant which exists in the industrial wastewater. Methylene blue dye (MB) is a cationic dye used in many textile manufacturer, and is a potential carcinogen(Ghaedi et al., 2015). It is used in different applications in biology, medicine, pharmaceutical, food, painting, and textile industries (Ginimuge et al., 2010). MB is recalcitrant, and difficult to biodegrade, so it is toxic to aquatic organisms, animals, and human beings. Due to their high solubility in water, MB dye cause contamination in aquatic ecosystems when discharged directly without treatment (Oz et al., 2011; Xu et al., 2014).

Dyes discharges in the aquatic body will prevent light penetration and photosynthesis in it. Due to their toxicity and non-biodegradability properties, dyes will causes environmental risks, and can be harmful to aquatic life and human beings. MB dye has various dangerous effects on humans and the environment, in which it causes high pulse rate, vomiting and nausea (El-Mekkawi et al., 2016; Li et al., 2016). MB dye is commonly found in industrial wastewater, and causes devastating effects on the aquatic environment.

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* Corresponding Author, Email: mnrashed@hotmail.com

Drinking water treatment sludge is discharged as waste from the coagulation process in a drinking water supply plant, as a result of adding alum (aluminum sulfate) to the water. Using this waste as adsorbent provides many benefits, in which it decreases the cost of removing pollutants from water, decreasing amounts of residuals which are accumulating in the environment, considered easily obtainable , and environmentally low cost material to utilize for the removal of pollutants from polluted water (Magdalena et al., 2019). This sludge was used as adsorbent to remove several dyes from wastewater (Hamid et al.,2017; Rashed et al.,2016a ;Mahesh et al.,2019).

Advanced oxidation processes (AOP) based on the generation of oxidizing free radicals, especially hydroxyl radicals, have been used due to their high oxidizing power (Yonar, 2011). Heterogeneous photocatalysis is one of the most AOP, that appears as a destructive technology leading to higher mineralization of most of the organic pollutants (Herrmannet al., 1999).Al-Shamali (2013) studied the photocatalytic degradation of methylene blue (MB) dye from water by photocatalysis process in presence of TiO_2 under solar radiation, and found that lower dye concentration leads to the highest degradation efficiency of MB. Shahin et al. (2016) prepared a novel nanofibrous composite made of Polyethersulfone (PES) for removal of methylene blue (MB) dye from polluted water, and shows that low isoelectric point of the polymer at elevated pHs can offer a high hydroxylated surface area for adsorption of cationic MB molecules. Mansour et al. (2016) prepared CuO nanoparticles, and used it for degradation of methylene-blue (MB), in which CuO nanoparticles exhibited a good photocatalytic activity in the degradation of the dye. Also, they reported that the catalytic degradation activity of MB dye exposed to the UV radiation was high at room temperature. Ong et al. (2012) studied a photocatalytic decolorization system equipped with immobilized TiO_2 to remove methylene blue dye under various operational parameters, and reported that the percentage of dye removal increased with increasing irradiation time. Salhi et al. (2015) studied photodegradation of methylene blue dye using titanium doped hydroxyapatite as catalyst in aqueous suspension, and found that a ratio of catalyst/solution was about 1 g/L. Yani et al.(2018) studied the adsorption of methylene blue dye on composite TiO_2 / alum sludge . Hamid et al.(2017) studied the adsorption of methylene blue from aqueous solutions using water treatment sludge modified with sodium alginate. Atout et al. (2017) studied photocatalytic degradation of methylene blue dye using TiO_2 supported on granular activated carbon.

One of the dyes treatment processes is the photocatalytic degradation. This treatment process has high efficiency in mineralization of organic pollutants. Titanium dioxide (TiO_2) in anatase form has been used for its high potential application in the degradation of several environmental pollutants (Mahmoodi & Arami, 2009). TiO_2 has a large surface area, and surface energy. As TiO_2 illuminated with light energy greater than the band gap energy ($\lambda < 380$ nm), it acts as a photocatalyst to mineralized toxic organic compounds from polluted solution. The main disadvantages of using the suspension form of TiO_2 were the post treatment catalyst recovery, and so immobilize TiO_2 onto solid supports were applied. Therefore, TiO_2 may be immobilized on the adsorbent from drinking water treatment sludge to obtain new composite. These new composite , with high surface area, can better adsorb and degrade organic pollutants in polluted water by photo assistance, besides, this composite is easily regenerated . So, it is the purpose of this study.

Also, the purpose of this study is to prepare a composite from drinking water treatment sludge, as a waste material, loaded TiO_2 , followed by investigating its photocatalytic degradation of methylene blue dye under UV radiation light and UV/H_2O_2.

MATERIAL AND METHODS

Titanium (IV) butoxide [Ti $(OC_4H_9)_4$], 97 %, cadmium stock standard solution (1000± 0.002 mg/L), and Methylene blue dye (chemical formula $C_{16}H_{18}ClN_3S$, 99.98 % purity) were from Aldrich, BDH and Merch Companies. All reagents and chemicals were highly analytically grade. The solution pH was adjusted with NaOH or HCl.

MB dye solution (1000 ppm) was prepared by dissolving 1gm of MB in 1000 mL of double distilled water. Working dye solutions were prepared by diluting the stock solution (1000 ppm).

The adsorbent from activated drinking water sludge was prepared as described in our previous study (Rashed et al., 2016 b). For physical activation of sludge, 100 g of the dry sludge was pyrolized at 700° C for 1h , the resulted adsorbent labeled ASP . For chemical activation, the dried sludge sample 10 g was mixed with 50 ml of 0.25 M HNO_3, filtered and left for 24 h. After that it was washed with deionized water, dried at 60 ^{o} C in an oven for 24 h and left in desiccators for further use (Rashed et al., 2016b), the resulted adsorbent labeled ASN Composites (ASP/TiO_2 and ASN/TiO_2) were prepared by the sol –gel method (Huang et al., 2008). Sludge adsorbents (ASP, ASN) were suspended in 30 ml of absolute ethanol and strongly stirred using magnetic stirrer, while 10 ml of titanium (IV) butoxide was added during stirring very slowly keeping the pH at 4. The resulting solution was stirred continuously for 2 h. Finally, deionized water and absolute ethanol mixture (1:1) was added drop wise till the gel was formed. The gel was aged overnight, dried at 100^oC for 6 h and calcinated at 450^oC for 4 h. The ratio of sludge adsorbent /TiO_2 was varied at 1:1, 1:2, and 2:1 by weigh.

The XRD pattern of the nanocomposites was analyzed using X-ray diffraction instrument (Philips, filtered Cu Kα radiation (n=1.5418 Å), 40 kV and 40 mA. The values of 2θ recorded from 4 to 79.82° 2θ with a scanning speed of 0.02°2θ per second. XRF is used for elemental analysis, where the percent of metals and metal oxides can be detected accurately even the traces. The instrument used is X-ray Fluorescence Spectrometry (EDXRF, JOEL JSX 3222). TEM (JEOL-JEM-1230, Tokyo, Japan, magnification power up to 600 kX, an acceleration voltage up to 200 kV, and resolution power down to 0.2 nm was applied to the structure of the prepared samples. Specific Surface Area (SSA) of the prepared samples was calculated according to BET using the N_2 adsorption –desorption capacity. The isotherms of the samples were recorded by the N_2 adsorption-desorption method using Quantachrome NOVA 2000 series Instrument (UK). Before measurement, the sample was degaussed at 300^oC for 2h, and the surface area was determined by the multipoint BET method using the adsorption data in the relative pressure range of 0.1 − 0.3.

The band gap energy was determined from the intersection of the tangent through the point of inflection in the absorption band and the photon energy axis. The sample spectra were recorded over a range of 200-800 nm using spectrophotometer (UV/vis near IR JASCO V-570) equipped with a Lab-spherical integrating sphere and $BaSO_4$ as a reference material. The band gap of the composites was calculated by converting the reflectance data to Kubelka-Munk units.

Schematic diagram of photocatalytic UV reactor is shown in Figure 1.
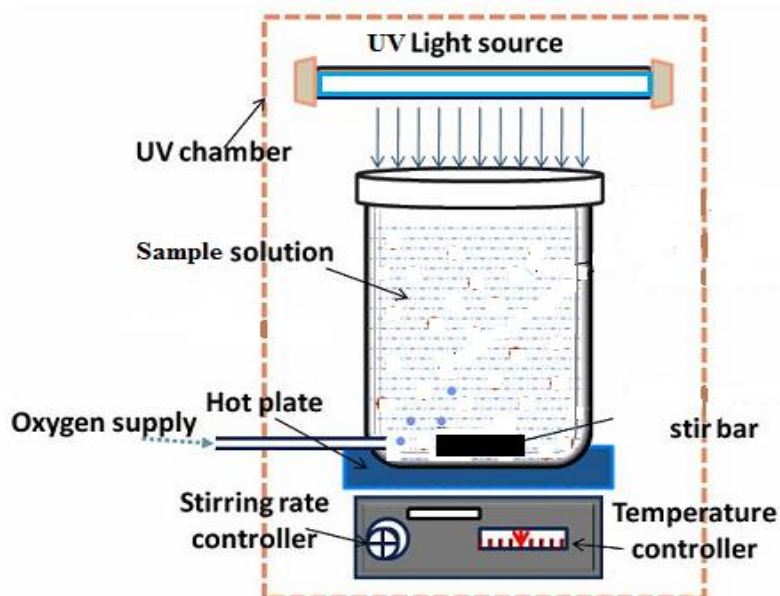
Fig.1. Schematic diagram of UV reactor

Photoreactor consists of multi magnetic stirrer, two UV irradiation lamps (UV-C G20 / T8, λ 253 nm) and draft chamber with air condition.

The photocatalytic activity of composites was evaluated by determining the efficiency and rate constant of MB degradation. 0.125 g of composite (ASP/TiO$_2$, ASN/TiO$_2$) was added to 50 ml of MB aqueous solution (50 ppm), and stirred in dark condition at room temperature (25°C) for 30 min to achieve degradation equilibrium of MB dye. Afterwards, the suspension was evaluated under UV-irradiation in the UV reactor. After the equilibrium irradiation time , the MB solution was separated by centrifuge and its concentration was analyzed using UV-Vis spectrophotometer at 664 nm . Photocatlytic activity tests were done in triplicate in all samples. The photocatalytic degradation efficiency was calculated using the following equation:

Degradation efficiency of MB (%) = (Co-Ct/Co)*100   (1)

where C$_o$, the initial concentration of MB, and C$_t$ is the concentration of MB at different irradiation time t (min) . For the effects of different parameters on dye decolorization , several experiments are conducted and discussed below.

To select the optimum composite according to MB dye removal degradation ,composites (ASP/ TiO$_2$, ASN/ TiO$_2$) with different adsorbent /TiO$_2$ ratios (1:1, 1:2 and 2:1) were applied for MB photocatalytic degradation at pH = 7, composite dose 0.125 g and 50 ppm initial dye concentration.

The effect of the MB dye concentration on decolorization was studied. Different concentrations (50, 60, 75, and 100 ppm) of MB dye were used at constant pH 7, composite dose 0.125 g and 4h irradiation time. The solution pH plays an important role in the MB dye degradation. The degradation efficiency of MB studied at four different pH values (3, 5, 7 and 9) was studied at constant conditions of dye concentration 50 ppm, catalyst dosage 0.125 g, and 4 h irradiation time degradation. The effect of composite loading on the MB degradation was investigated using the 0.05, 0.125 and 0.25 g of composite with remaining of all other parameters constant (pH= 7, dye concentration 50 ppm ,and 4 h irradiation

time. The effect of irradiation time on the rate of MB dye photocatalyst degradation was studied at selecting the optimum conditions of composite dosage 0.125 g, pH 7 and dye concentration 50 ppm .The irradiation time was varied from 30 min to 240 min under UV irradiation. H_2O_2 is one of the strong agents used in the degradation of azo dyes in the present study. The effect of H_2O_2 on the removal efficiency of MB dye was studied by adding 1 ml H_2O_2/L under UV irradiation for 4h.

RESULTS AND DISCUSSION

The chemical composition of the prepared adsorbents (ASN and ASP), and composites (ASN/TiO$_2$ and ASP/TiO$_2$) were investigated by XRF and summarized in Figures (2 and 3). From the Figures the intensity of the titania TiO$_2$ peak in the composite samples (ASN/TiO$_2$ and ASP/TiO$_2$) increased as the ratio of the added titania increased. Also, the resulted XRF chemical analysis showed the differences in titania and carbon percentage between the adsorbents(ASN, ASP) and the composites(ASN/TiO$_2$ and ASP/TiO$_2$). So, this result confirmed the presence of high TiO$_2$ in the composites.
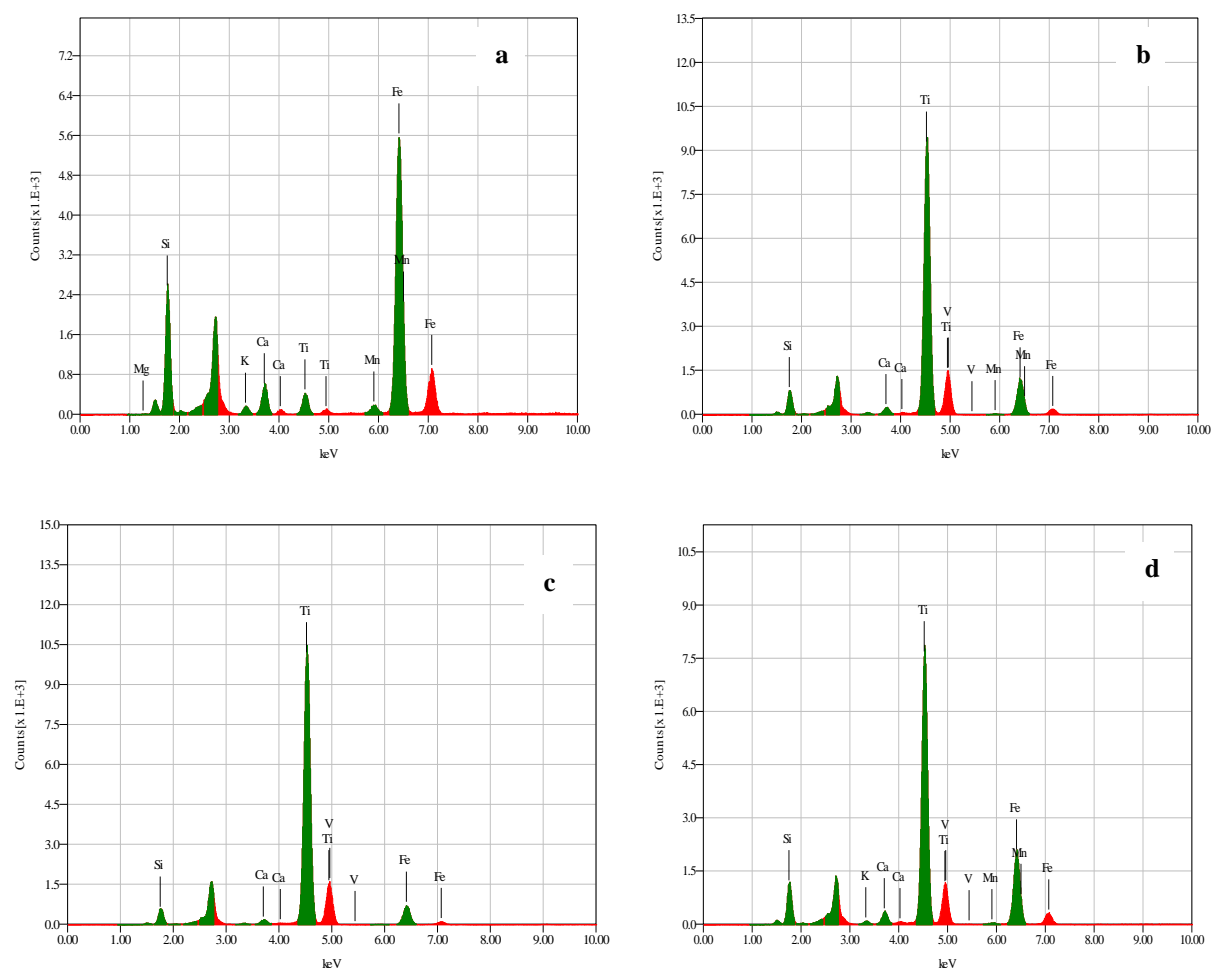

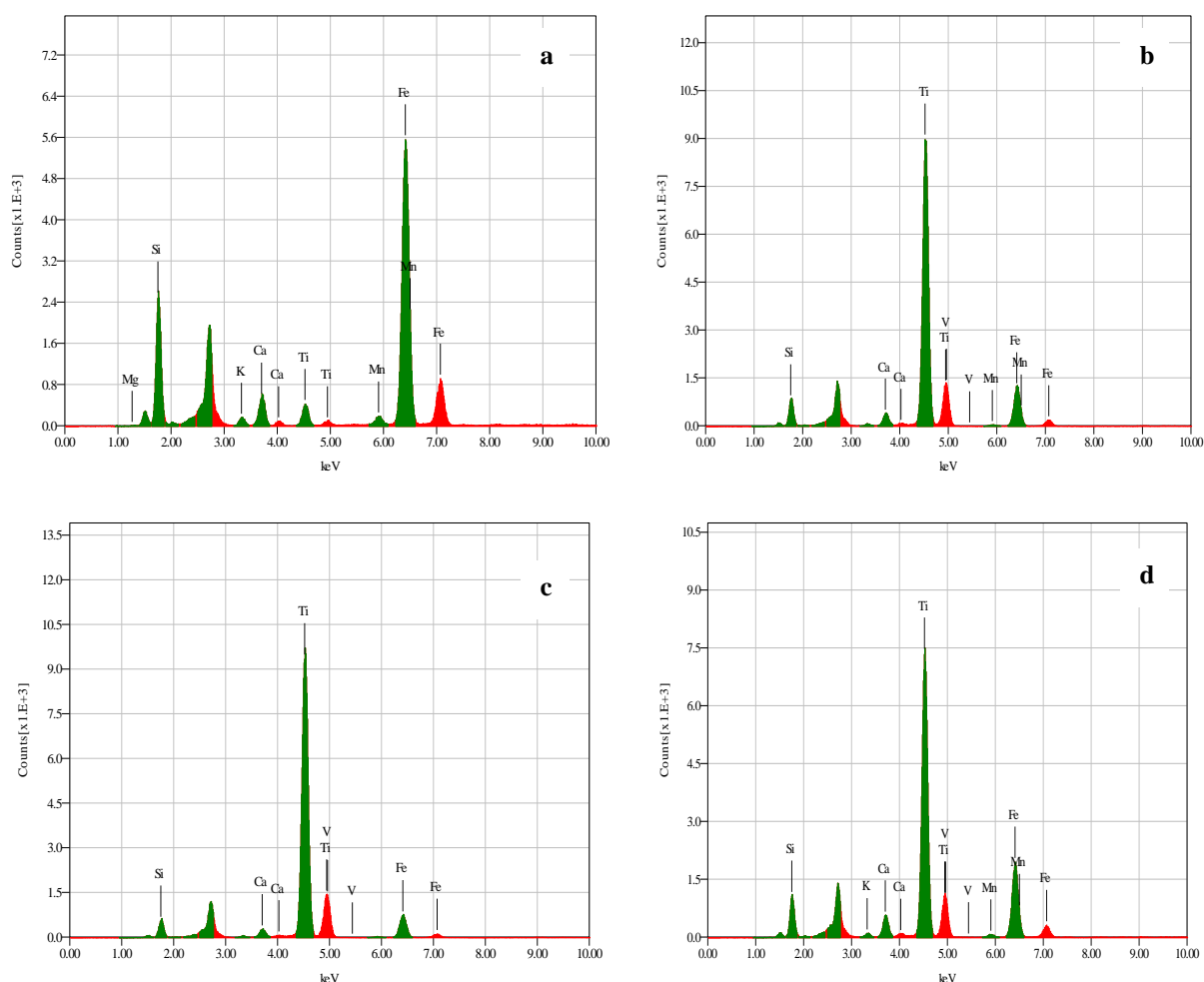Fig. 2. XRF of (a) ASN, (b) ASN/TiO$_2$ (1:1), (c) ASN/TiO$_2$ (1:2) and (d) ASN/TiO$_2$ (2:1).

Fig. 3. XRF of (a) ASP, (b) ASP/TiO$_2$ (1:1), (c) ASP/TiO$_2$ (1:2) and (d) ASP/TiO$_2$ (2:1).

XRD patterns of adsorbents (ASN, ASP), anatase TiO$_2$, and the composites (ASN/TiO$_2$, ASP/TiO$_2$) are shown in Figures 4 and 5.

The XRD pattern of the adsorbent and composite samples is shown in Fig.4. The XRD pattern of alum sludge nitric adsorbent (ASN), and alum sludge pyrolized adsorbent (ASP) show the peaks corresponding to quartz, microcline, calcite and albite minerals. After loading with TiO$_2$, the prepared alum nitric composite (ASN/TiO$_2$), and alum pyrolized composite (ASP/TiO$_2$) new diffraction peaks appeared in 25.3^o, 37.96^o, 47.99^o , 54.3^o, 55.4^o,62.8^o, and 68.9 ^{o} (Ba-Abbad et al., 2012). These results indicate the presence of the introduced TiO$_2$ in the prepared composite ASN/TiO$_2$ and ASP/TiO$_2$.

The crystalline size was determined by Scherer's equation. The results showed that, the crystalline sizes of ASN /TiO$_2$ were 3, 9.8, 13.3 and 59 nm, and for ASP/TiO$_2$ it were 5.3, 29.7, 58.3 and 120 nm.

ASN/TiO$_2$ composite was selected for characterization with TEM; because of its higher removal efficiency than ASP/TiO$_2$ composite. TEM gives the particles shape and size on the scale of atomic diameters (Gao & Elder, 2000). Figure 6 shows typical TEM images of ASN/TiO$_2$ composite. The figure (6) shows that titania particles were well dispersed on the surface of ASN/TiO$_2$, with particle size in the nanometer scale range. Also, it reveals that the morphologies of sample consist of hexagonal-like particles of sludge (caly) , accompanied by a spherical smaller particle of titania.
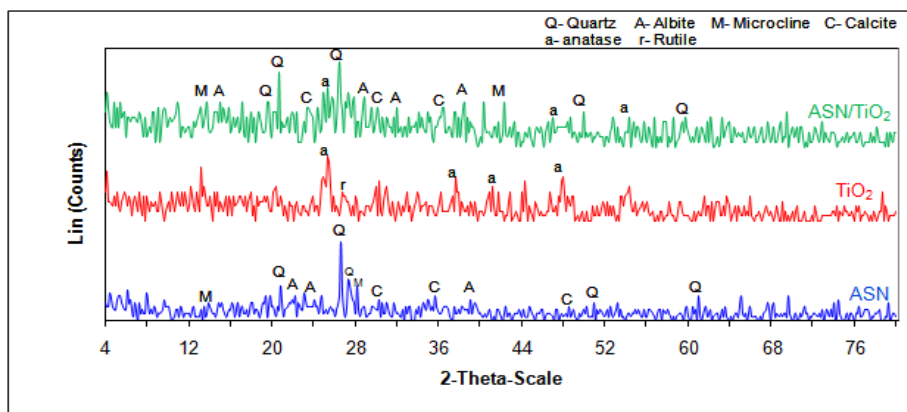
Fig. 4 . XRD spectrum of alum sludge nitric adsorbent (ASN), the nanotitania (TiO₂) and alum sludge nitric composite (ASN/TiO₂).
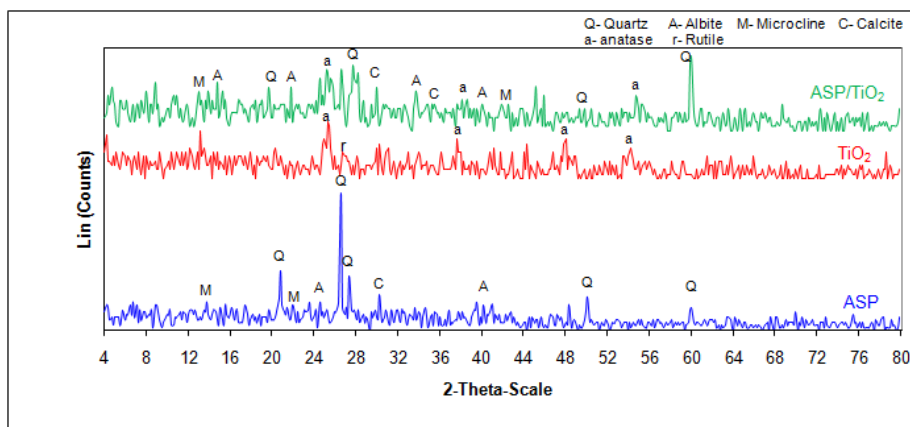

Fig. 5. XRD spectrum of alum sludge pyrolized adsorbent (ASP), nanotitania (TiO₂) and alum pyrolized composite (ASP/TiO₂).
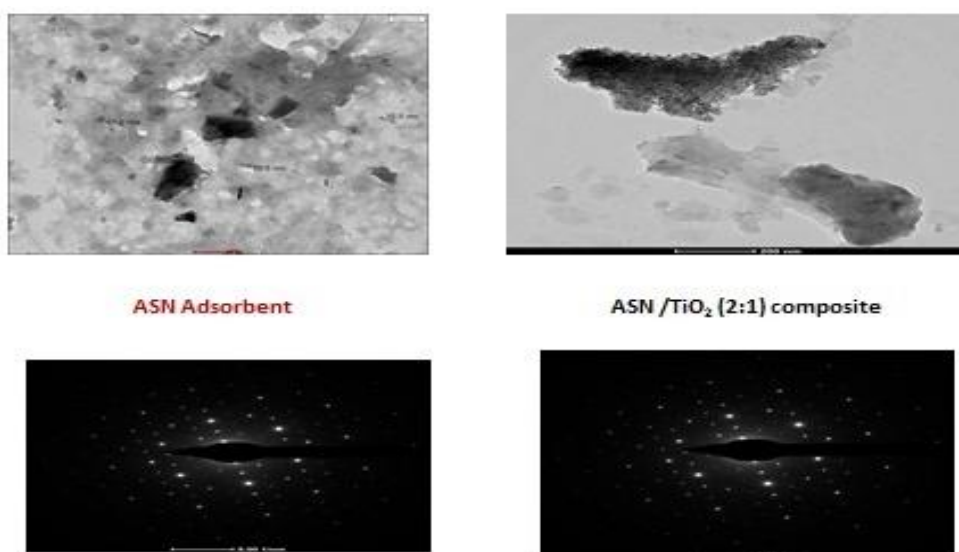

Fig. 6. HR-TEM image of ASN adsorbent and ASN/TiO₂   composites , with selection electron diffraction pattern (SEAD).

Surface area and pore size of the adsorbent (ASN) and the composite (ASN/TiO$_2$) was estimated by the BET method , and presented in Table (2). It was found that the surface area value for alum adsorbent (ASN) was 50.97 m^2/g, while that for the composite (ASN/TiO$_2$) it was 82.46 m^2/g. These results indicate the increase of the surface area of the prepared composite than that of the corresponding adsorbent. The pore size distribution is obtained by application of the BJH (Barrett-Joyner-Halenda) method for the desorption isotherm of the samples. Table (1) shows the pore size of ASN adsorbent 17.14 nm , and that for alum sludge composite ASN/TiO$_2$ is 16.55 nm.

The values of the band gap of sludge adsorbent and its composite were measured by (F (R) hv)$^{1/2}$ method. Table 1 showed the band gap of ASN and ASN/TiO$_2$ composite. The results illustrated the band gab energy's values of ASN and ASN/TiO$_2$ were 3.32 and 3.12 ev, respectively. The decrease in band gap was due to the low value of TiO$_2$ band gap (3.06 ev) (Zhang et al., 2011). Therefore, the decrease of band gap facilitates its application under visible light.

The results for selecting the optimal highly effective composite (Table 2) indicated that the best ratio of the prepared composites for high degradation (using UV) and adsorption (in the dark) of MB was that with ASN/TiO$_2$ (2:1). This is due to the increasing of the amount of sludge adsorbent which leads to the increase of the surface area. The photodegradation of MB by UV irradiation with the composites were in the order : (ASP , ASN) /TiO$_2$ (2:1) > (ASP , ASN) /TiO$_2$ (1:1) > (ASP , ASN) /TiO$_2$ (1:2). The increase of the sludge adsorbent on the composite surface leads to more photocatalytic degradation active sites or may be due to direct contact between the dye and the surface of sludge adsorbent which facilitate degradation.

Optimum conditions for the degradation efficiency of MB Dye. The effect of initial MB dye concentration on the Efficiency of Photocatalytic Degradation was shown in Figure (7). The MB degradation efficiency increased as the MB dye concentration decreased. This reveals that the MB removal (95.7% with ASN/TiO$_2$, 86.58% with ASP/TiO$_2$) was the highest at low MB dye concentration (50 ppm). The decrease in the degradation resulted at higher MB dye concentration (100 ppm), and this may be due to that the MB dye molecules need to be adsorbed on the composite surface and occupying the active sites at high dye concentration. In addition, as the amount of dye molecules increase, the light penetrating of the dye solution to reach the composite surface is reduced (Susheela, 2012).

Table 1. Pore size, surface area and band gap energy of adsorbent and composite

Adsorbents and nanocomposites	BET surface area (m2/g)	Pore size (nm)	Average pore volume (cm3/g)	Band Gap (ev)
Alum sludge adsorbent ASN	50.97	17.14	0.02184	3.32
Alum sludge composite ASN/TiO2	82.46	16.55	0.03412	3.12

Table 2. Degradation of MB dye by composites under UV irradiation and in dark.

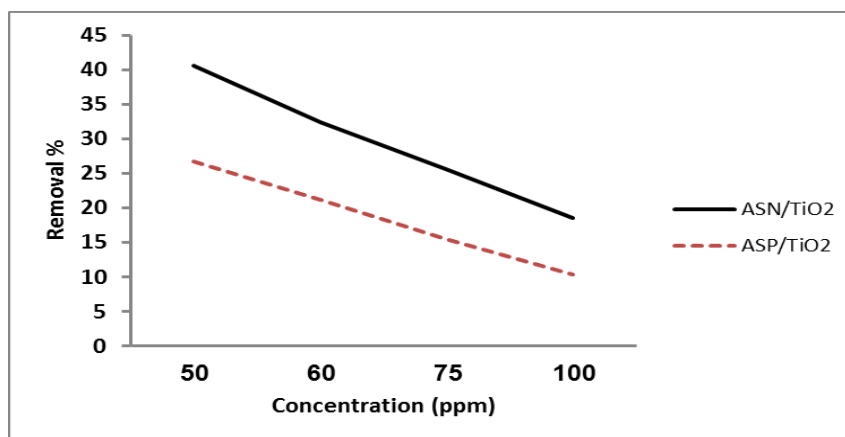| Composite	% Dye removal on dark	% Dye Removal with UV
ASN /TiO$_2$ (1:1)	22.4	82.8
ASN/TiO$_2$ (1:2)	20.2	80.4
ASN/TiO$_2$ (2:1)	23.6	88.5
ASP/TiO$_2$ (1:1)	20.4	78.6
ASP/TiO$_2$ (1:2)	17.8	73.9
ASP/TiO$_2$ (2:1)	21.0	81.5

Fig. 7. Effect of intial dye concentration on the degradation of MB dye

Yani et al. (2018) studied the removal of methylene blue dye from wastewater using adsorbent from alum sludge and found that MB removal increased with the decrease of MB concentration, and this agreed with our results. The results by Reza et al. (2016) agreed with our results; where the decolorization of MB dye was higher at low MB dye concentration , and also other results agreed with our results (Yang et al., 2015; Rache et al., 2014 ; Bousala, 2012). Mushtaq et al. (2016) studied TiO_2 photocatalytic degradation of MB dye by UV light as the radiation source. Ong et al. (2012) found that dye degradation decreases as the dye concentration increases. Ankita et al. (2013) studied the effect of photocatalytic degradation of methylene blue over ferric tungstate, and reported that the degradation rate decreased with an increase in the concentration of dye further. Marziyeh et al. (2012) reported that the removal of methylene blue with TiO_2 nanopowder was high at a lower initial concentration of MB dye. Kumar et al. (2016) studied the photocatalytic degradation of methylene blue dye on Ag-Ag_2O/TiO_2 polypyrrole and found that 100% degradation of MB was observed at lower MB dye concentrations with UV and visible light irradiation. Al-Shamali (2009) reported that the photocatalytic degradation efficiency of MB dye in the presence of TiO_2 catalyst assisted solar radiation decreases with dye concentration up to 25 mg/L after 90 min irradiation time.

The results of the MB degradation at different pH values (3, 5, 7, and 9) was represented in Figures (8). The photocatalytic degradation of MB dye increased as the solution pH increased. The MB degradation increases from 58.36% to 97.22% as pH increases from 3 to 9 using ASN/TiO_2, and from 46.12% to 89.45% using ASP/TiO_2.

The increase of MB degradation rates may be due to the increase of hydroxyl ions at higher pH value, which generates more hydroxyl radicals by combining with holes, that considered responsible for the photocatalytic degradation (*Almeida, 2009*). Above pH value 7, more hydroxyl ions will compete with the electron rich MB dye for adsorption on (ASP , ASN) /TiO_2 composite surface.

Yani et al.(2018) found that pH 11 suitable for high degradation of MB using alum sludge/TiO_2 adsorbent, and this agrees with our results. Rather et al. (2017) studied the photocatalytic MB degradation by plasmonic metal-TiO_2 nanocatalysts under visible light irradiation, and found that the effect of pH on the photocatalytic degradation of MB increase in pH from 3 to 10. This result was agreed with the present study.

The MB degradation rate was affected by the composite dosages. The results

(Fig.9) show that as the composite dose increased from 0.05 to 0.25 g, the removal efficiency of MB increased from 70.25% to 97.25% using ASN/TiO$_2$, from 58.25% to 91.88% using ASP/TiO$_2$; this is because of the increase of the number of available adsorption site by an increase in composite dose, as well as the reduction of inter-particle emission (Leili et al, 2013).These results concluded that the phtocatalytic degradation of MB dye was highly effective with 0.25 g composite.
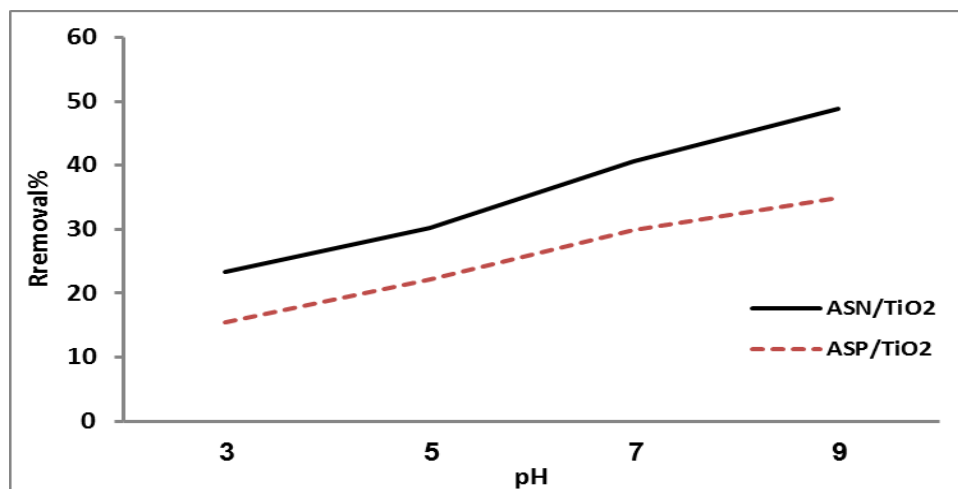

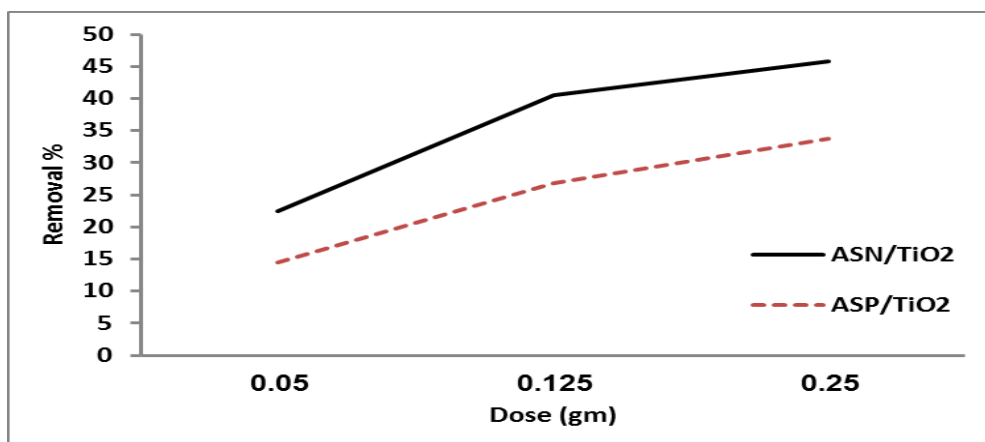**Fig. 8. Effect of pH on the degradation of MB dye**

Fig. 9. Effect of composite dosage on the MB degradation

The increase in MB degradation with the increase of the composite dosages was due to the increase of the active sites on the surface of the composite . Rather et al. (2017) found that the degradation of MB was high (100 %) at 1.2 g/L TiO$_2$ catalyst dose . Salhi et al. (2015) reported that the degradation of MB dye increased with increasing catalyst (titanium-doped hydroxyapatite) amount (1g/L). Salehi et al.(2012) studied the influence of the removal of MB with TiO$_2$ nanopowder and found that the MB degradation efficiency increases with increasing the catalysis dosage 0.2 g/L. Al-Shamali (2013) ended for that the MB degradation efficiency, increased as TiO$_2$ dose increased from 1 to 2 g/L, and the complete degradation of MB (100%) was at 90 min irradiation time.
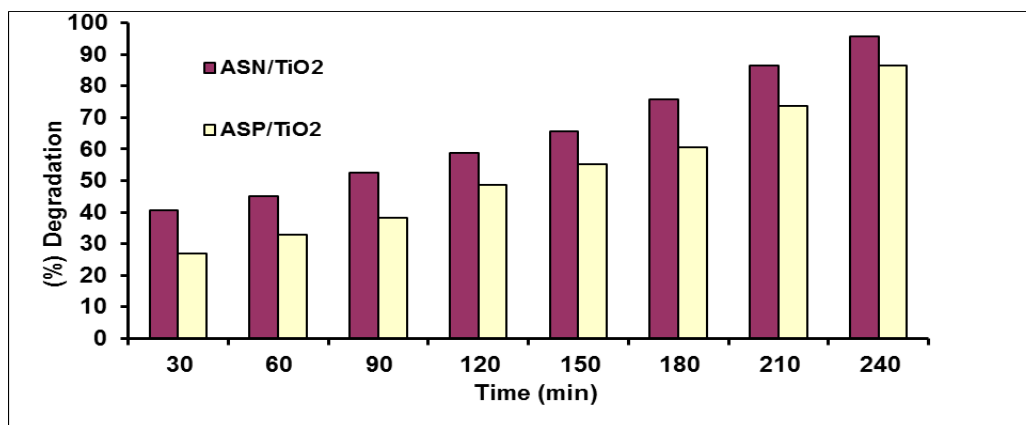
Fig. 10. Effect of irradiation time on the photocatalytic degradation of MB dye

The data reported from the effect of UV irradiation time on the photocatalystic degradation of MB dye was presented in Figure (10). Results revealed that with the increase of irradiation time, the absorption intensity of MB gradually decreased, indicating the degradation of MB under the used condition. The maximum degradation of the MB dye was after 4 h UV irradiation. This increase is due to the fact that as time increases the bond between different molecules of MB dye appears to be weaker, and the chromophore part of the molecule breaks down. The UV irradiation on MB solution in the presence of composite (ASP/TiO$_2$, ASN/TiO$_2$) resulted in a decrease in the intensity of the absorption spectrum; this is because more hydroxyl radicals will be generated at the longer UV exposure time, which is crucial in the photocatalytic degradation process as it oxidizes the organic pollutants to CO$_2$, simple mineral acids and water (Ong et al.,2012).

Devadi et al.(2014) studied a photocatalytic degradation of MB dye on immobilized TiO$_2$, and found that the degradation percentage increases as the irradiation time increases to maximum degradation efficiency at 80 min. Atout et al.(2017) reported maximum photodegradation of MB on TiO$_2$/ granular activated carbon after 250 min under UV irradiation.

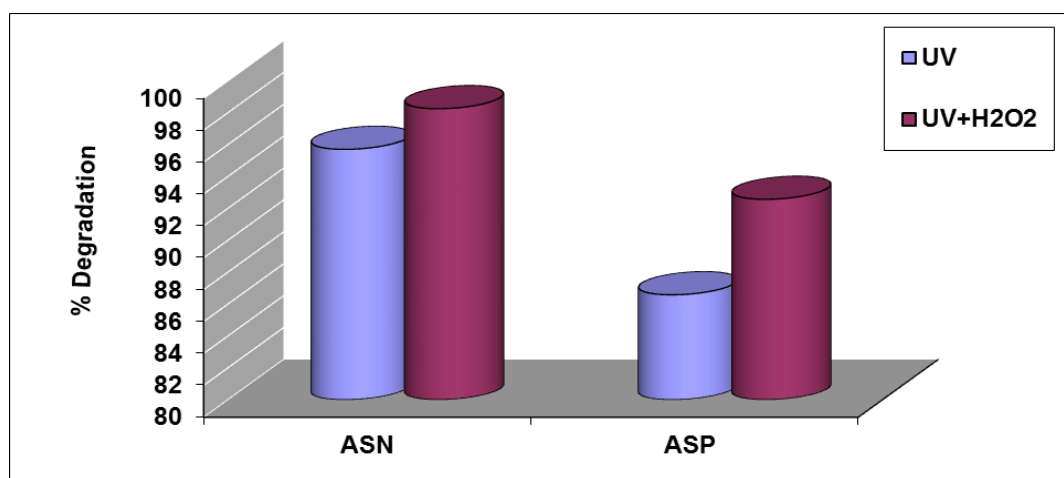Figure (11) represented the effect of H$_2$O$_2$ on the photocatalytic degradation of MB dye.

Fig. 11. Degradation of MB dye using the prepared composites under UV and UV/H$_2$O$_2$

Results reveal that the degradation of MB dye was a maximum with 1 ml H_2O_2/L dye solution. The removal efficiency of MB dye increased when H_2O_2 was used in the presence of UV radiation; because the free hydroxyl radicals are generated by the dissociation of H_2O_2 in the presence of UV radiations (Bhattacharyya & Sharma, 2005), and the high concentration of H_2O_2 act as scavenger itself, which decrease the hydroxyl radicals that reducing compound elimination (Legrini et al.,1993).

Investigation of the kinetics of MB dye photodegradation under UV-light irradiation is shown in Table 3. The kinetic plots of MB degradation on the composite under UV-irradiation is shown by pseudo-first order reactio.

$$r = dc/dt = kC \qquad (2)$$

r, is the reaction rate, k is the apparent rate constant and C the concentration of MB in the aqueous solution. The rate constants calculated by the equation.

$$In\ (Co/Ct) = kt \qquad (3)$$

Where Co is the initial concentration of MB dye and Ct is the concentration of MB at various contacts time , and t is the irradiation time. k is the apparent pseudo-first order rate constant.

By plotting ln Co/Ct versus irradiation time (t) will obtain the reaction rate constant (k) which is the slope of fitted lines. The results (Table 3) indicated that the photocatalytic degradation of MB dye followed the first-order kinetic. The calculated rate constants (k) of MB

degradation using ASN/TiO$_2$ and ASP/TiO$_2$ composite under UV light for 240 min are 0.0091 and 0.0065 min^{-1}, respectively (Table 3). The data reveal that the degradation rate of ASN/TiO$_2$ composite is 2.12×10^{-2} µm min^{-1} was higher than that for ASP/TiO$_2$, which indicated that ASN/TiO$_2$ composite has the highest photocatalytic activity under UV irradiation.

The sustainability and reuse of the composite (ASP/TiO$_2$ and ASN/TiO$_2$) was studied at constant experimental parameters, and repeated the photcatlytic experiment for five sets with a fresh MB solution at each set.

MB loaded the composite was mixed with the regeneration solution of 1% HCl in water and stirred for 60 min. The solid material was separated, washed with high pure deionized water in order to remove any organic contamination due to MB. The composite was applied in repeated five consecutive MB adsorption cycles. The results show a good sustained of the composites (ASN /TiO$_2$, ASP/TiO$_2$) after subject to the five regeneration cycle of MB degradation. Only small losses of their photodegradation activity were observed after the fifth cycle as presented in Figure (12), So that it could be used for several times effectively.

Makama et al. (2015) studied the stability of CdS and TiO$_2$ catalyst for photocatalysis of MB dye by recycling degradation tests , and found that a good MB removal efficiency (85.9%) was on the first run.

Table 3. Kinetic parameter of the first- order kinetic reaction for the photocatalytic degradation of MB with composites

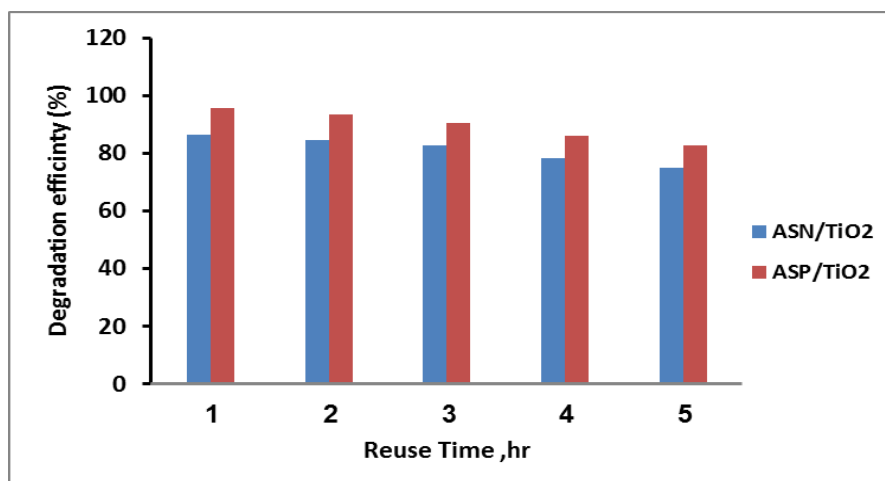| Composite	% Degradation efficiency	K, Reaction rate constant (min^{-1})	Initial reaction rate r_o*10^{-2} (µMmin^{-1})	Correlation coefficient, R^2
ASN/TiO$_2$	95.7	0.0091	2.12	0.8912
ASP/TiO$_2$	86.58	0.0065	1.72	0.8698

Fig. 12. Stability and reusability of the prepared composites

CONCLUSION

The present composites (ASN /TiO$_2$, ASP/TiO$_2$) were successfully prepared from drinking water treatment sludge , as a waste, and TiO$_2$ nanopartile by sol-gel method . The prepared composites were characterized by TEM, XRD, XRF, BET and surface area . The prepared composites were successfully used for photocatalytic degradation of MB dye under UV. Maximum degradation of MB dye was at 4 h UV irradiation time, 50 ppm initial dye concentration, solution pH=7, 1mL H$_2$O$_2$ and 0.125 g composite dosage. Stability and reusability of the composites show that the degradation was slightly decreased by repeated use after the fifth cycle. So that it could be used for several times effectively. The future research must focus on the preparation of nano adsorbents with high surface area and degradation of the pollutant.

GRANT SUPPORT DETAILS

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research

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