World Applied Sciences Journal 19 (6): 874-879, 2012
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2012.19.06.1644

Photocatalytic Degradation of Kermanshah Refinery Wastewater Using Nano-TiO_2 Supported on Bentonite

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Abstract: TiO_2/bentonite nanocompoite were prepared by sol gel method. XRD, BET, EDX and SEM were used to characterize the prepared photocatalyst. The methods confirmed the deposition of TiO_2 on bentonite. Loading the TiO_2 increased the surface area of the composite comparing to pure TiO_2 and bentonite. The photocatalytic properties of nanocomposite was tested in degradation of a waste from a refinery plant and it was compared with pure titania and bentonite with and without UV irradiation. Titania loaded nanocomposite has the greatest activity comparing the others. Increasing the catalyst weight and temperature led to increasing the photocatalytic degradation percent. GC analysis of the sample in optimum condition showed that the prepared photocatalyst can degrade efficiently all of the organic pollutants were present in the waste, in 4 h.

Key words: Photocatalyst % Nano-TiO_2 % Sol-Gel, Bentonite

INTRODUCTION

Organic pollution arising from various industries is a challenging issue nowadays and finding an efficient way to treat these types of wastes has a great importance. Advanced oxidation processes (AOPs) have been used in past decades as a promising technology for degradation of such a pollutant. Mineralization of the organics in this technology proceeds by highly reactive hydroxyl radical attack and since it has no selectivity, the method can be used for wide range of organic contaminants. Among the semiconductor, TiO_2, because of its high photocatalytic activity, stability, low price and non-toxicity is far superior candidate [1-5].

A large number of researches have been done to investigate the photocatalytic activity of TiO_2 considering its structure and size [6-11]. Most of studies have been done on anatase and rutile phases of nanostructured TiO_2, while scarce reports are demonstrated on brookite [12].

The phototocatalyst can be used as suspension in wastewater or immobilized on inert surfaces. Using the photacatalyst as suspension needs a recovery step after the reaction, but coating the catalyst on a porous material can avoid the step, resulting in saving the energy and cost. Moreover TiO_2 particles aggregate in suspension, resulting in small surface area, lower catalytic activity and complicating the filtration of suspensions, which makes the photocatalytic process impractical [13].

Several immobilization methods such as spray coating, sputtering, dip coating, electrophoretic deposition and sol–gel related have been proposed and various support such as activated carbon, quartz, glass beads, stainless steel, silica, aluminum and etc. have been studied [14].

In this study we investigated the degradation of Kermanshah Refinery wastes using bentonite supported TiO_2 as catalyst. The most significant pollutants in this wastes are aromatics, however other pollutants are present in the wastes. Conventional biological treatment methods are ineffective for degradation of these pollutants and unfortunately, there are no universally useful methods available for treatment of these wastes. In recent years, AOPs have been considered as a promising method for degradation of these wastes as demonstrated [15].

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MATERIALS AND METHODS

Materials: The experimental involved following steps: preparation of bentonite, synthesis of TiO_2/bentonite and photo-degradation of the Kermanshah Refinery waste to investigate the photocatalytic properties of the prepared catalyst.

To activate the bentonite, it was rinsed with distillated water. As it was expected the bentonite absorbed the water and swelled, so the impurities settled down faster than it. Then the slurry was centrifuged and the bentonite was separated. It was dried at 104°C for 12 hours in an oven. HCl solution (8 M, 1:5 w/v) was added to the bentonite powder and it was activated below 70°C for 3 hours, filtrated, washed with double distillated water (to remove the excess acid) and dried at 104°C for 12 hours. The obtained powder was milled, sieved with a 270-mesh sieve and mixed with a 20% NH_3 solution (1:4 w/v). After stirring at room temperature for 12 hours, the mixture was filtrated, washed again to remove the residual ammonia and dried at 80°C for 16 hours. After the activation process the specific surface area increased to 83 m^2/g.

Sol-gel method using titanium tetraisopropoxide was used in this research to synthesize the catalyst. 25 ml of alkoxide solution was added drop by drop to 500 ml solution of double distillated water and isopropyl alcohol (v/v ratio of 9:1), with vigorous agitation. Then the pH was adjusted at 2 using nitric acid. The mixture was agitated vigorously at 70°C for 24 hours and the stable titania sol was formed.

To synthesize the TiO_2/bentonite nanophotocatalyst a 4% slurry of ammoniaed bentonite was prepared and 500 ml of it was loaded to the reactor. It was agitated vigorously for 1 hour for maximum absorption of water by bentonite and its efficiently swelling for separation of the layers. Then 50 ml of titania sol was added and agitated at room temperature for 24 hours. It was filtrated and washed to remove the excess titania. The product was dried at 100°C for 12 hours and then was calcined at 400°C for 2 hours.

The UV lamp (UV-C, 200 W) was used to irradiate the waste with initial COD (Chemical Oxygen Demand) of 700 ppm. The waste was for gasoline production unit and its pH was between 6.5 to 7.5 and its turbidity was about 100 NTU. Reactor volume was 1 L. Digestion systems was used for the determination of the COD.

Characterization: The qualitative identification of nanocomposite sample phases was made by powder X-ray diffraction (PXRD) technique. X-ray diffraction measurement was used and it was done on a STOE STADI MP X-ray diffractometer using Cu K" radiation (8 = 0.15406 nm). EDX was also used for elemental analysis of the sample. The surface area was measured by BET method, using a Coulter 100 CXO nitrogen adsorption apparatus. The nitrogen adsorption-desorption isotherms of the samples were determined by N_2 adsorption at 77 K. The microporous area was obtained from the t-plot of N_2 adsorption data at higher partial pressures. SEM was used to observe the formed composite particles and the second phase precipitated on support.

Catalytic activities of samples were determined by degradation of a Kermanshah Refinery waste sample provided by a factory in Kermanshah province of Iran. Natural bentonite, commercial TiO_2 nanopowder and the composite were used for degradation of the waste in various pHs, catalyst weight and temperatures. The concentrations were detected using a Cary UV-Vis spectrometer.

RESULT AND DISCUSSION

Table 1 shows the EDX analyses of samples prepared using various volumes of titania sol to load the titania on bentonite. It can be observed that with increasing the volume of the used sol, the amount of the loaded titania is increased from about 11 up to 24%. Figure 1 shows that the loading percent of titania is about to be saturated in 24%. Excess amount of titania is removed by washing.

Figure 2 shows the XRD pattern of pure anatase and titania loaded bentonite. It can be seen that anatase peaks at 25.48°, 38.24°, 48.12°, 54.96° and 63.48° are present in titania loaded bentonite. XRD pattern shows that the TiO_2 deposited on the surface of bentonite has not the cristallinity of the pure one.

Figure 3 shows the SEM of TiO_2/bentonite photocatalyst. It can be seen that the particles are formed in various sizes. TiO_2 particles can be observed on the surface of bentonite. The particles have not ordered forms.

By coating the TiO_2 on bentonite the surface area of the nanocomposite was increased and reaches to 219 m^2/g. Other parameters are presented in Table 2 and Figure 4. The surface area of commercial nano-TiO_2 was 152 m^2/gr. Increasing the surface area leads to increase the exposed surface of photocatalyst and consequently increasing the activity of photocatalyst, which results in faster degradation of pollutants.

Table 1: EDX Analysis of nanocomposite prepared using various volume of titania sol

Volume of titania sol (ml)	15		20		25		30		35	
Element	W t%	At %	W t%	At %	W t%	At %	W t%	At %	W t%	At %
Mg k	1.35	1.79	1.01	1.15	0.93	1.02	0.83	0.91	0.80	0.97
Al k	10.70	12.81	9.18	10.70	7.84	8.41	7.10	7.33	6.89	6.95
Si k	57.89	65.20	55.25	63.15	54.12	62.30	52.91	61.06	52.30	60.54
K k	1.39	1.06	1.30	1.03	1.18	0.94	1.03	0.84	0.61	0.57
Ca k	1.07	0.75	0.91	0.61	0.75	0.57	0.69	0.51	0.55	0.49
Ti k	14.32	11.15	18.36	15.19	21.06	18.42	23.10	20.56	24.36	21.20
Fe k	4.41	5.37	10.01	5.87	10.10	5.93	10.21	6.01	10.29	6.27
Cu k	3.87	1.87	3.98	2.03	4.02	2.41	4.13	2.73	4.20	3.01
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 2: BET analysis of the composite

Vm(cm^3/gr)	Total pore volume (cm^3/gr)	Mean pore diameter (nm)	BET (m^2/gr)
50.183	0.3137	5.74	219

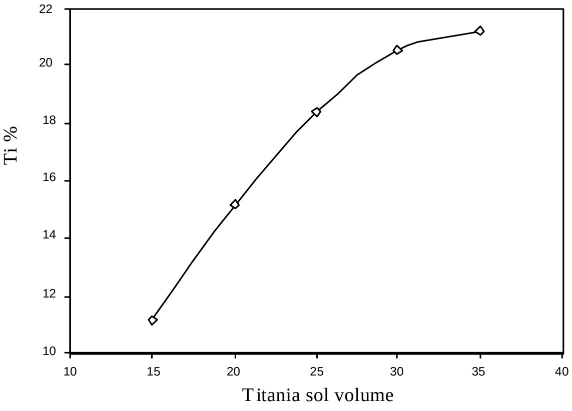


Fig. 1: Ti percent absorbed on bentonite

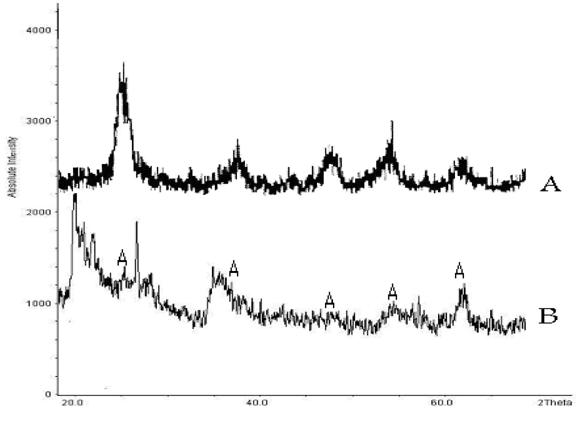


Fig. 2: XRD pattern of pure TiO_2 (A) and TiO_2 loaded bentonite (B)

To investigate the photocatalytic activity of prepared nanocomposite a waste from the refinery plant of Kermanshah with COD of 700 ppm was exposed to the nanocomposite, commercial nano-TiO_2 and natural bentonite with UV irradiation. The concentration was measured using UV-Visible spectrometry. It can be observed in Figure 5 that using pure bentonite leads to concentration decrease of about 30% and the prepared nanocomposite decrease about 50% of the pollutant, but the nanocomposite degrades about 90% of the pollutants. The concentration decrease without UV irradiation can be because of adsorption. Since the nanocomposite has higher surface area rather than the pure bentonite, its adsorption property is greater. Comparing the photocatalytic activity of nanocomposite and commercial nano-TiO_2 revealed that the nanocomposite has greater activity than the others. It can be attributed to the smaller surface area of commercial nano-TiO_2.

The effect of catalyst weight on degradation percent can be observed in Figure 6. The figure shows that increasing the catalyst weight increases the degradation percent; but the cost and separation problems should be considered for increasing the catalyst weight.

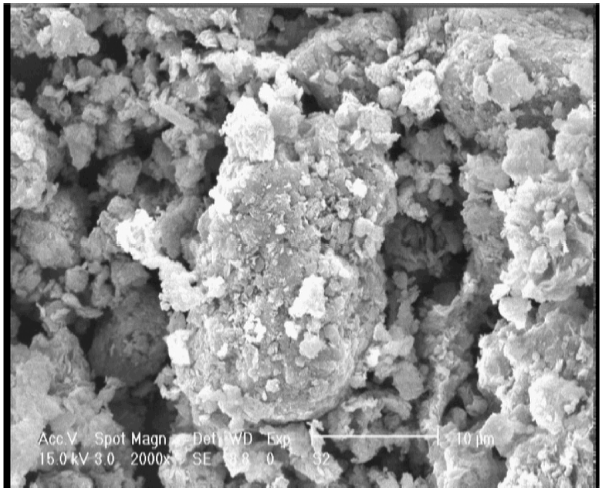
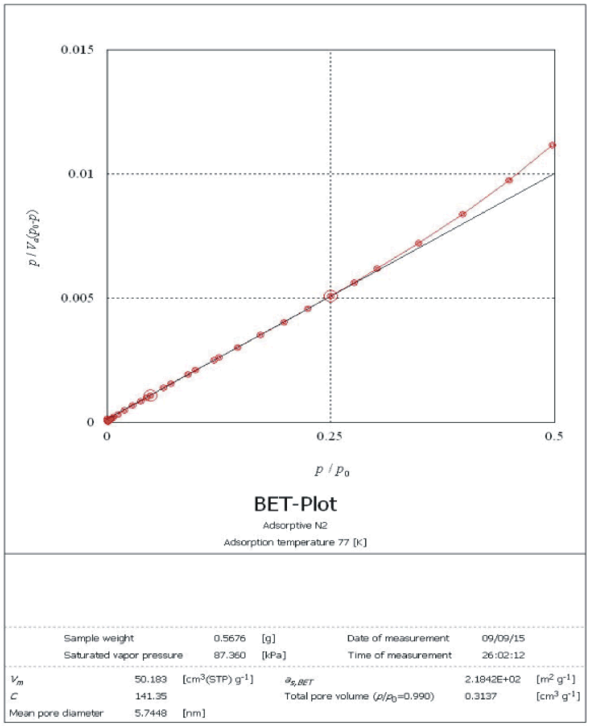


Fig. 3: SEM photograph of TiO_2/bentonite



Sample weight	0.5676	[g]	Date of measurement	09/09/15	
Saturated vapor pressure	87.360	[kPa]	Time of measurement	26:02:12	
V_m	50.183	[cm^3(STP) g^{-1}]	$a_{s,BET}$	2.1842E+02	[m^2 g^{-1}]
C	141.35		Total pore volume (p/p_0=0.990)	0.3137	[cm^3 g^{-1}]
Mean pore diameter	5.7448	[nm]			

Fig. 4: N_2 adsorption isotherm of TiO_2/bentonite nanocomposite

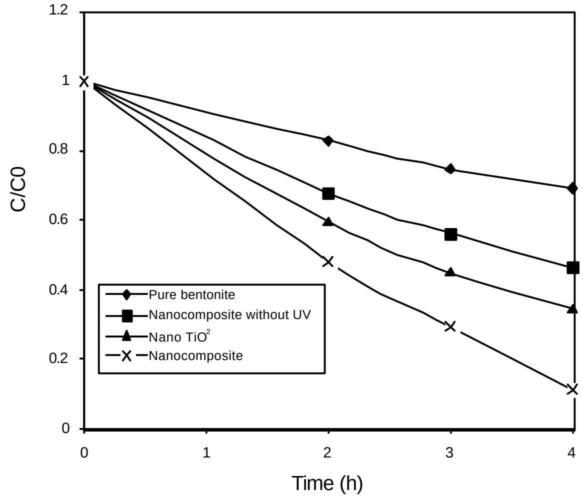


Fig. 5: Degradation ratio of the waste by UV irradiation in pH=4.5 and 1 g/L of catalyst

Temperature variation has also some effect on degradation percent. To investigate its effect three various temperatures were opt which were controlled before and during the reaction. We found out that increasing the temperature had a positive effect on degradation percent. It can be because of increasing the intensity of excitation by increasing the temperature and increasing the rate constant according the Arrhenius equation. Although the amount of adsorption decreases with an increase in the reaction temperature, the photocatalytic reaction competes more effectively with an electron-hole recombination and thus the photocatalytic reaction rate enhances [16]. We didn't increase the temperature to higher degrees because of considerable evaporation at high temperatures. Figure 7 shows the temperature effect on degradation percent.

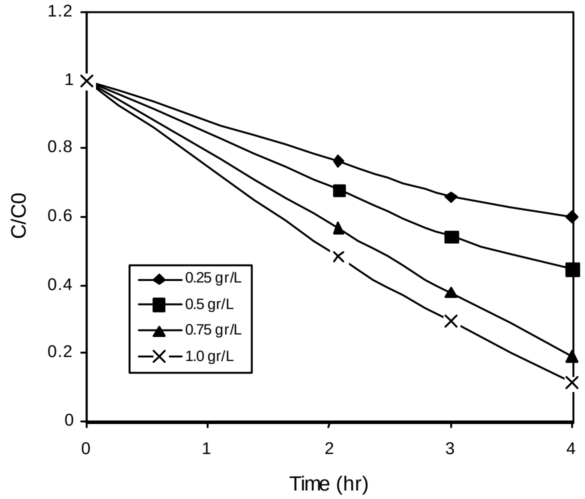


Fig. 6: Degradation ratio with various amounts of TiO_2/bentonite, pH=4.5, T=25°C

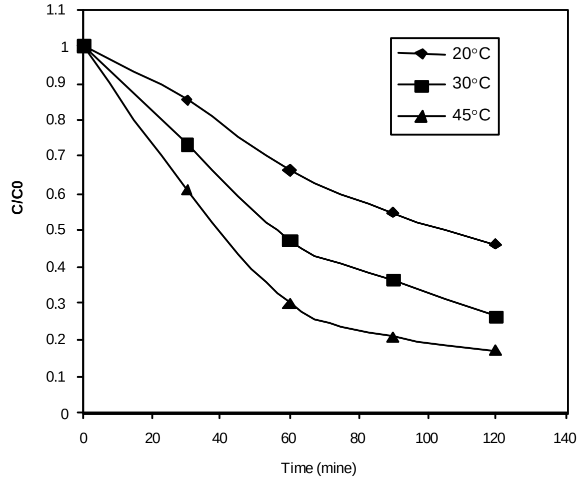


Fig. 7: The effect of temperature variation on degradation percent in pH=4.5 and 1 g/L of TiO_2/bentonite

The efficiency of the procedure in 4 h can be concluded from Figure 8. It shows the GC analysis of the waste obtained from Kermanshah Refinery Plant before the photocatalytic degradation in graph A and its composition after photocatalytic degradation in graph B.

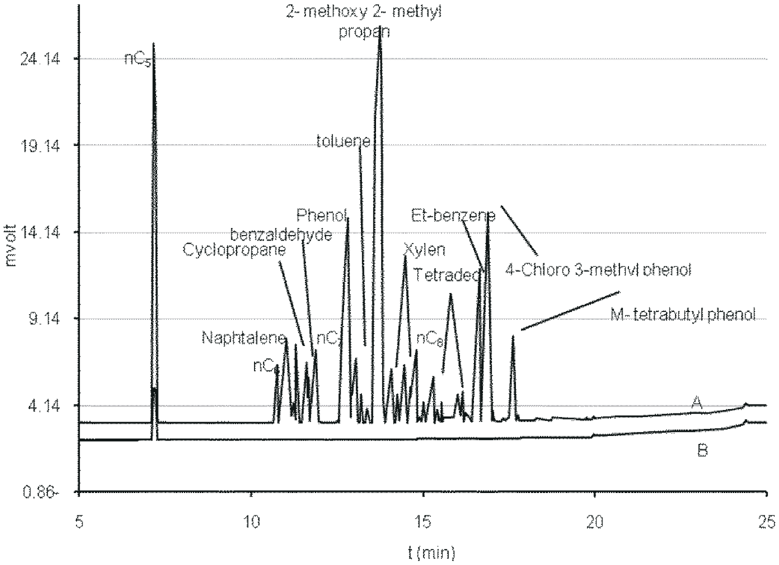


Fig. 8: Comparing the waste composition before (A) and after (B) degradation using GC analysis in pH=4.5 and 1 g/L of TiO_2/bentonite

It is obvious that the photocatalytic degradation procedure has high efficiency and all of the organic compounds presented in the waste, were degraded in 4 h.

CONCLUSION

TiO_2/bentonite nanocompoite were prepared by sol gel method. It was characterized by XRD, BET, EDX and SEM. Loading the TiO_2 led to increase the surface area of the composite. The composite was used for photocatalytic degradation of a waste from Kermanshah Refinery Plant and the results were compared with pure titania and pure bentonit with and without irradiation of UV light. Titania loaded nanocomposite has the greatest activity Increasing the catalyst weight and temperature led to increasing the photocatalytic degradation percent. GC analysis of the sample in optimum condition showed that the prepared photocatalyst can degrade efficiently all of the organic pollutants were present in the waste, in 4 h.

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