Modification of Titanium Dioxide for Wastewater Treatment Application and Its Recovery for Reuse

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Abstract: Magnetic Fe_3O_4 nanomagnetic particles were synthesized by the titration co-precipitation method followed by coating by the sol-gel method with Titanium dioxide. The photocatalytic activities of different synthesized $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanomagnetic particles with different molar ratios of TiO_2 to Fe_3O_4 were investigated by the reduction of phosphate, nitrate and decolorizing of methyl blue solutions. X-ray diffraction was used to characterize the size, composition and morphology of the synthesized particles. The results obtained from these experiments indicate an increase in the photocatalytic activity as the amount of TiO_2 coating increases. The results show a higher activity of the synthesized particles in the removal of phosphate, nitrate and methyl blue, which can be achieved at early reaction periods at about 70-80%. The activities were higher when the particles were incubated without UV illumination. This study shows that $\text{TiO}_2/\text{Fe}_3\text{O}_4$ particles are effective in phosphate, nitrate and methyl blue removal in wastewater treatment.

Key words: Photocatalysis, nanomagnetic particles, phosphate, nitrate, methyl blue, co-precipitation, wastewater treatment, X-ray diffraction.

1. Introduction

Water pollution has been a major problem faced by many countries. The availability of clean and safe drinking water has also been a prior concern by many developing countries. There has been an increasing demand of fresh and clean water due to the depletion of most water resources by the growth in population, extended droughts and pollutants from many industrial wastes [1, 2]. More than five (5) million people die each year from water related diseases and about 2.3 billion more suffer from diseases related to the drinking of contaminated water. However, 60% of child mortality cases in the world are also related to infectious and parasitic diseases from polluted water [3].

The processes in the treatment of wastewater generally comprise of several stages that target the

removal of dissolved and particulate water pollutants. Wastewater treatment is an important component in environmental management and as such the use of appropriate and cost effective methods in the treatment of all kinds of wastewater is essential in achieving environmental sustainability.

The general wastewater treatment consists of two main processes: the Primary stage, where large objects such as sticks, stones and rags are removed, and the biological treatment process, where the wastewater is purified by removing most of the contaminants. This study is focused on the secondary stage process with the use of Titanium nanoparticles as the catalyst for the detoxification process.

Nanotechnology has been employed in recent years for the purification of water as it is highly effective in the detoxification of pollutants and germs found in contaminated water resources. The use of nanoparticles, nanomembranes and nanopowders has been the major focus for today's wastewater treatment processes for removal of biological, chemical and

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organic compounds. The effectiveness of nanotechnology to other existing techniques in water purification is as a result of the high surface to volume ratio and hence the ability to reach all targeted compounds in the water [4].

Titanium nanopowders have recently received much attention in the application of the treatment of wastewater. Studies show that Titanium nanopowders are very effective in this application but a question on the recovery of the powders after the reaction process has been a major topic for researchers in the nanotechnology field [5]. These Titanium nanopowders are applied in the purification process by a process known as Photocatalysis. The term photocatalysis is the use of light to activate a catalyst to increase the reaction rate of a particular process [6]. The use of TiO_2 nanoparticles in wastewater purification processes has been a major research effort in the field of photocatalysis due to its ability to decompose organic compounds and its high stability [7]. The excellent large energy gap of Titanium dioxide makes it a very important semiconductor with an energy gap of 3.2 eV [8-10].

This study aimed at the synthesis of TiO_2 nanoparticles with an inner magnetic (Fe_3O_4) core and the application of these nanoparticles in phosphate, nitrate and dye removal from wastewater through Photocatalysis. The TiO_2 synthesis was carried out in two steps: the preparation of Fe_3O_4 nanoparticles by the co-precipitation method and TiO_2 coating by the sol-gel method [9, 11, 12].

Phosphorus enters municipal wastewater treatment works from both domestic and industrial sources, with typical concentrations between 4 and 12 $\text{mg}\cdot\text{L}^{-1}$, which must be reduced before it is discharged into the environment [9, 13].

2. Materials and Methods

2.1 Synthesis of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ Nanomagnetic Particles

2.1.1 Materials and Chemicals

The materials and chemical used are listed below:

(1) 97% Titanium (IV) butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$) – TBOT

- Molar mass (TBOT) = 340.32 g/mol

(2) 99% FeCl_2 , 99% FeCl_3 , Ammonia, 0.1M HCl, Ethanol, Double distilled water.

Wastewater samples were received from Henriksdal in Stockholm, Sweden.

2.1.2 Titration Co-precipitation Method

The synthesis of Fe_3O_4 nanomagnetic particles was carried out by adding 100 mL of $0.015 \text{ mol}\cdot\text{L}^{-1}$ FeCl_2 aqueous solution and 200 mL of $0.015 \text{ mol}\cdot\text{L}^{-1}$ FeCl_3 aqueous solutions (1:2 stoichiometry of Fe^{2+} and Fe^{3+} ions). The solution was well mixed and placed in a water bath at 40 °C and vigorously stirred. Ammonia was then dropped into the mixture slowly and drop wise until a pH of 9 was attained. The presence of the formation of large black precipitates at a pH = 9 indicate the generation of Fe_2O_4 magnetic nanoparticles. It is important to have an oxygen free environment during the process of synthesis, since magnetite can be further oxidized to ferric hydroxide in the reaction medium in the presence of oxygen.

These nanoparticles were then washed several times with a mixture of ethanol and distilled water and then separating the particles with a magnetic stand or by centrifuging until the pH dropped to about 7. The particles were then suspended in water. Eq. (1) is the overall reaction equation:

2.1.3 Coating the Fe_3O_4 Nanomagnetic Particles with TiO_2 by Sol-gel Technique

An amount of the suspended Fe_3O_4 nanomagnetic particles in water was again dissolved in a mixture of ethanol and water of the ratio 20:1 respectively. The mixture was ultra-sonicated at a higher intensity for about 10 minutes to ensure homogeneity. A 0.1 M HCl was dropped into the mixture until the pH is about 4-5. The mixture was then placed in a water bath at about 40 °C. Different volumes of 97% Titanium (IV) butoxide (TBOT) were dissolved by

adding ethanol and acetic acid simultaneously until a homogeneous mixture was obtained. The dissolved TBOT was then slowly dropped into the mixture while vigorously stirring. The stirring was continued for about 45 minutes to ensure homogeneity. The composites were then separated by a magnetic stand or centrifuging and later washed several times with ethanol and water until a pH of 7 [14].

The chemistry of coating by the sol-gel method:

The coating of the Fe_3O_4 with TiO_2 produced a “core-shell” structure. According to Alkhateeb [15], the synthesis of nanoparticles with the core-shell structure by the sol-gel method results in a structure with covalent, van der Waals forces, electrostatic forces or hydrogen forces holding the inner core to outer shell (Fig. 1).

2.1.4 Drying and Calcination

For characterization purposes, the nanomagnetic particles are dried in an oven at 70 °C.

After coating, the particles were aged for 6 hours and then dried in the oven at 70 °C, followed by calcining at 450 °C.

2.1.5 Calculations

The concentrations (mg/mL) of synthesized particles of different amounts of the precursor were used to coat fix concentrations of Fe_3O_4 .

$$[\text{TiO}_2/\text{Fe}_3\text{O}_4] = \frac{(\text{empty container} - \text{empty container filled with sample}) (\text{mg})}{\text{volume of sample (mL)}} \quad (2)$$

The Photocatalytic activity test on prepared samples of different concentrations of TBOT for the synthesis of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs can be calculated as Eq. (3):

$$\begin{aligned} \text{Relative removal} \\ (\text{Activity}) (\%) = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100 \quad (3) \end{aligned}$$

2.2 Photocatalysis Activity Investigation

The synthesized $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs were applied on standard prepared solutions of phosphate dissolved in

Fig. 1 Core-shell structure of the synthesized $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

deionised water. It was also applied to wastewater samples for the reduction of total phosphate, total nitrate and dye removal using Ultraviolet spectrophotometer screening.

2.3 Characterization of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs

2.3.1 X-Ray Diffraction

The X-ray diffraction method is a versatile, non-destructive technique that shows detailed information about the crystallographic structure of materials.

2.3.2 The XRD Technique

The dried analyzed $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and Fe_3O_4 magnetic particles were finely ground, homogenized into very fine powders and placed in a holder. The sample was then illuminated with x-rays at a fixed wave-length of and the intensity of the reflected radiation recorded. This data was then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units- 10^{-8} cm), showing concentric rings of scattering peaks corresponding to the various “D” spacing in the crystal lattice. This technique is the powdered diffraction method; this is the mostly used X-ray technique for the characterization of materials of single crystalline domain randomly oriented. The peak positions and intensities are used for the identification of the phase of the analyzed material [15]. Fig. 2 shows the mechanism of X-ray diffraction.

$$D = 0.9\lambda / \beta \cos\theta \quad (4)$$

where

Fig. 2 Mechanism of X-ray diffraction.

D : the size of the particles of the analyzed sample.

λ : the wavelength of emitted X-ray.

β : full width at half maximum of the corresponding XRD peak patterns.

θ : diffraction angle.

The system was run at 45 kV, 40 mA and 2θ data collected at a steady scan rates beginning at 20° and ending at 70° .

3. Results

3.1 Reactive Phosphorous

Fig. 3 shows a standard plot of different concentration of phosphate and their absorbance using spectrophotometer analysis at 890 nm wavelength [16].

Fig. 3 Standard curve for phosphate test.

The activities of the synthesized nanopowders of different concentrations of TBOT coatings of the Fe_3O_4 magnetic nanoparticles at different time were made and the activity of the reduction in the initial concentrations of phosphate was evaluated. These evaluations were used to determine the activity of the different synthesized particles for better process optimization. From the result shown in Fig. 4, it can be noticed that the average “activity” of the reduction of phosphate by the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs is about 50% over all the standard prepared concentrations.

Fig. 5 shows the results of a test using a waste water sample. These tests were carried out using two distinct applications. Firstly, the test was carried out under UV illumination (photocatalysis), and secondly, under no UV illumination. Both tests were carried out on two wastewater samples (outlet and inlet). It can be noticed from the graph that the reduction of phosphate in the wastewater was very effective using the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs. The inlet wastewater has a higher phosphate concentration as compared to the outlet. The inlet wastewater shows a drastic reduction in phosphate concentration after the incubation period with the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs (Fig. 5).

The results on the activities of 26.3 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs at 30 minutes incubation using both UV and no UV illumination is presented in Table 1.

Fig. 4 Total Phosphate reduction on standard prepared solutions using 11.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Fig. 5 Total phosphate reduction in the wastewater after 30 minutes incubation using 26.3 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Table 1 Phosphate reduction (Activity) at 30 minutes by 26.3 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Test	Activity (%) inlet w/w sample	Activity (%) outlet w/w sample
UV illumination	96.8	55.6
No UV illumination	96.3	55.5

The results of the total phosphate reduction test in wastewater samples 11.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs is presented in Fig. 6.

The reductions in the phosphate concentrations using 11.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs concentration were also significantly high in the inlet wastewater as well as the outlet. Values of the activities are shown in Table 2.

The results of the total phosphate reduction test in wastewater samples using 8.0 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs at an incubation period of 30 minutes is shown in Fig. 7.

The reductions in the phosphate concentrations using $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs concentration of 8.0 mg/mL were also significantly high in the inlet wastewater as well as the outlet wastewater. Values of the activities are shown in Table 3.

It can be concluded that the activity of the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs for the reduction of Phosphate depends on the concentrations of Titanium(IV) butoxide (TBOT) coating on the Fe_3O_4 magnetic nanoparticles. The higher the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs concentration is, the higher the activity of the nanoparticles are and vice versa. The reduction is also

Fig. 6 Total phosphate reduction in the wastewater after 30 minutes incubation using 11.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Table 2 Phosphate reduction (Activity) at 30 minutes by 11.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Test	Activity (%) Inlet w/w sample	Activity (%) outlet w/w sample
UV illumination	86.1	44.4
No UV illumination	84.3	22.2

Fig. 7 Total phosphate reduction in the wastewater samples at 30 minutes incubation using 8.0 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Table 3 Phosphate reduction (Activity) at 30 minutes by 8.0 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Test	Activity (%) inlet	Activity (%) outlet
UV illumination	86.1	33.3
No UV illumination	83.8	33.3

very effective in samples of higher concentrations of phosphate than those at lower concentrations.

The results of the total phosphate reduction test on wastewater samples using 41.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs is presented in Fig. 9.

For Fig. 8, the analysis was performed using a much higher concentration of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs (41.5 mg/mL).

The test was also performed using shorter incubation times in order to evaluate the rate of reaction (Activity) of the nanoparticles with time (Table 4).

From the calculated activities of the synthesized Fe_3O_4 and $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs, it can be concluded that the reductions of phosphate takes place at an early period. A higher activity is achieved even after 5 minutes

Fig. 8 Total phosphate reduction in w/w samples using 41.5 mg/mL TiO₂/Fe₃O₄ MNPs for time experiment.

Table 4 Phosphate reduction (Activity) with respect to time using 41.5 mg/mL TiO₂/Fe₃O₄ MNPs.

Time (minutes)	5	10	15	20	25	30	40	45	60
Activity (%)	93.3	95.0	96.7	97.5	98.3	98.3	97.8	97.5	97.8

Fig. 9 Standard curve for phosphate test.

of incubation. Comparing to the previous run, it can also be established that a higher activity is attained when the concentration of the TBOT is increased.

3.2 Reactive Nitrate

Fig. 9 shows a Standard curve for Total Nitrate test at a 500 nm wavelength using a Spectrophotometer analysis at 890 nm wavelength (Blake and D.M., 2001). The cadmium Reduction Method HR (0 to 30.0 mg/L NO³⁻_N) analysis range using a 10 mL Nitra Ver 5 Nitrate Reagent powder pillow for the analysis of nitrogen was also used.

The activities of synthesized 26.3 mg/mL TiO₂/Fe₃O₄ MNPs nanoparticles in the reduction of the nitrate concentrations in untreated wastewater samples (inlet sample) and treated wastewater samples (outlet sample) at two different incubation periods (15 and 30 minutes) were investigated. The effect of UV illumination was also examined to determine the effect of UV on the synthesized particles. The results obtained are as shown in Fig. 10 and Table 5.

The results show that about 70-80% reductions were obtained at higher concentration of nitrate, but it is also observed that, there is much effect of UV

illumination for the reduction of nitrates in lower concentrations. The results also establish the fact that the efficiency of the synthesized nanoparticles is much observed at lower concentrations than at higher concentrations.

The activity of a higher concentration of TBOT (41.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs) was also investigated on the treated wastewater sample (outlet) at much longer incubation periods to evaluate the effect of the TBOT concentration of the reduction of

nitrate at longer incubation periods under UV illumination. The results obtained as shown in Fig. 11 and Table 6.

The obtained results show that higher activity is achieved on the nitrate reduction at higher concentrations of TBOT. Higher activity of the synthesized particles could be observed at shorter incubation period. Higher activities are achieved at longer periods but the reduction is even evident at a shorter incubation time.

Fig. 10 Total nitrate reduction test using 26.3 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Table 5 Nitrate reduction (Activity) at 15 and 30 minutes by 26.3 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Test	Activity (%) inlet w/w sample (15 minutes)	Activity (%) outlet w/w sample (15 minutes)	Activity (%) inlet w/w sample (30 minutes)	Activity (%) inlet w/w sample (30 minutes)
UV illumination	73.5	81.4	75.5	80.3
No UV illumination	72.0	37.8	70.7	45.5

Fig. 11 Total nitrate reduction by 41.5 mg/mL $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Table 6 Nitrate reduction (Activity) at 15 and 30 minutes by 26.3 mg/mL TiO₂/Fe₃O₄ MNPs.

Test	Activity (%) outlet w/w sample (5 minutes)	Activity (%) outlet w/w sample (10 minutes)	Activity (%) outlet w/w sample (20 minutes)	Activity (%) outlet w/w sample (60 minutes)
UV illumination	83	88	97	98

3.3 Dye Removal Using TiO₂/Fe₃O₄ MNPs

Fig. 12 shows a test performed using methylene blue of different concentrations of (0.08% of 20% stock solution dissolved in 1,000 μ L deionized water) as a colored compound. Synthesized 26.3 mg/mL TiO₂/Fe₃O₄ MNPs were added and incubated at 30 and 60 minutes incubation periods and the activity of the nanoparticles was investigated at a 500 nm wavelength using a Spectrophotometer analysis at 890 nm wavelength [16]. The effect of UV illumination was also examined. The results obtained are shown in Fig. 12 and Table 7.

Samples

(1) Control sample volume: 20 μ L of 0.08% methylene blue dye, 1,000 μ L deionized water.

(2) Sample A volume : 20 μ L of 0.08% methylene blue dye, 1,000 μ L deionized water, 100 μ L of 26.3 mg/mL TiO₂/Fe₃O₄ MNPs.

(3) Sample B volume : 15 μ L of 0.08% methylene blue dye, 1,000 μ L deionized water, 100 μ L of 11.5 mg/mL TiO₂/Fe₃O₄ MNPs.

(4) Sample C volume: 10 μ L of 0.08% methylene blue dye, 1,000 μ L deionized water, 100 μ L of 8 mg/mL TiO₂/Fe₃O₄ MNPs.

The results obtained show evidence of the effect of UV illumination on the activity of the nanoparticles. The activities of the synthesized particles also increase during longer incubation periods. It can be concluded that the TiO₂/Fe₃O₄ MNPs were effective in the decolorization of methyl blue.

Fig. 13 shows an investigation of the activity of synthesized nanoparticles of 41.5 mg/mL TiO₂/Fe₃O₄ MNPs. This experiment was performed under UV illumination.

Control: 1 μ L of 0.08% methylene blue dissolved in 1,000 L distilled water.

Absorbance of control = 0.047.

Fig. 12 Dye removal by TiO₂/Fe₃O₄ MNPs.**Table 7 Nitrateate reduction (Activity) at 0-60 minutes by 26.3 mg/mL TiO₂/Fe₃O₄ MNPs.**

Test	Sample A 30 min	Sample B 30 min	Sample C 30 min	Sample A 60 min	Sample B 60 min	Sample C 60 min
UV illumination	58	54	67	77	72	92
No UV illumination	54	43	53	64	59	68

Fig. 13 Absorbance Vs time on dye removal by $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

Table 8 Concentrations of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs and their properties.

Volume of TBOT used for coating (μL)	Conc. of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs after drying (mg/mL)	Comments
100	8.0	Very good magnetic recovery, easy settling when in suspension and very small particle size. This shows the coating was very poor.
150	11.5	Good magnetic recovery, slightly soluble in suspension, this shows a slightly good coating.
250	26.3	Good magnetic recovery, very soluble in suspension. Good coating.
500	41.5	Weak magnetic recovery, very soluble in suspension. Large particle size, very good photocatalytic activity.

It was observed that, there is an activity of about 60% after 10 minutes of incubation. After 15 minutes, there seems to be a rise in the absorbance. This might be due to poor or bad separation of the nanoparticles before the absorbance value was analyzed. However, the activity increases as the incubation time increases.

Table 8 shows the Concentrations of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs and their properties.

3.4 Characterization of Synthesized Particles

The XRD spectra of the synthesized nanoparticles are shown in Figs. 9 and 10. The crystalline structures of the synthesized Fe_3O_4 and $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs were identified by X-ray diffraction. The peaks of the pure Fe_3O_4 MNPs appear to be higher or broader (peaks 311, 220 and 440), indicating that these particles are much smaller than the coated particles. There has been more peaks in the X-ray image of the coated MNPs ($\text{TiO}_2/\text{Fe}_3\text{O}_4$), (i.e. peaks a(101), a(004), a(200), a(211), a(116)). Comparing the two images, it appears

that the peaks reduced when the TiO_2 particles were coated on the Fe_3O_4 MNPs.

4. Discussion

The synthesis of TiO_2 photocatalytic particles with an inner superparamagnetic Fe_3O_4 was carried out successfully with the particles having good magnetic properties using the titration co-precipitation method followed by the sol-gel method. Normally, to have a good activity with photocatalytic particles, they should be illuminated with a UV lamp during the reaction process. But the synthesized particles were seen to have a higher activity during the reduction of phosphate blue even when they were not illuminated under UV lamp. This means the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs were active under visible light due to the introduction of the magnetic Fe_3O_4 inner core.

The Photocatalytic process has been mainly used in the destruction of organic compounds (alcohols, carboxylic acids, phenolic derivatives, or chlorinated

Fig. 9 X-ray image of pure synthesized Fe_3O_4 magnetic nanoparticles.

Fig. 10 X-ray image of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ MNPs.

aromatics) into carbon dioxide, water, and simple mineral acids which are very harmless to both human and the environment [17, 18].

In addition to the removal of organics, the photocatalytic surface of TiO_2 has also shown photochemical transformations in the reduction of inorganic compounds like; nitric oxides, azides, chlorate or bromated, halides, palladium and sulphur species [16, 19, 20]. TiO_2 is used for immobilizing these compounds on other surfaces of thin films [17].

In recent years, immobilizing TiO_2 particles on magnetic nanoparticles has been a major field in the photocatalysis field to optimize the activity and the separation of the TiO_2 powders from the reaction medium after the reaction process. There have been two general commercially available forms of TiO_2 used in Photocatalysis for the purification of water; the particles in suspended liquid media and the particles immobilized on thin films of glass beads. The reduction in the surface-volume ratio is the main

factor to consider since this affects the photocatalytic activity of the particles [18].

TiO₂/Fe₃O₄ MNPs were synthesized by the sol-gel method and these particles showed about 80% activity after irradiation time of 60 minutes. When these particles were recycled, they also showed tremendous photocatalysis activity even after reuse [4].

The results from this research show that the activity of the synthesized particles in the removal of phosphate, nitrate and methyl blue can even be achieved at early reaction periods at about 70-80%. The activities of the photocatalytic particles were higher when the particles were incubated without UV illumination. At lower concentrations of the TiO₂/Fe₃O₄ MNPs, the photocatalytic activity of the particles was higher enough. This can be said to be very cost effective since the application of the particles can be in smaller concentration. Further, the synthesis process is simple and an easy technique.

The synthesized TiO₂/Fe₃O₄ MNPs were easily recovered by a magnetic stand when they were used in suspension during all the experiments. The recovery of the particles was noticed to be faster when the particles have a lower concentration than when the concentrations are higher. This can be due to the inhibition of the magnetic core material by the TiO₂ coating. As the concentration of the surface coating increases the magnetic properties of the particles also decreases.

5. Conclusion

The activity of the particle was seen to greatly depend on the molar ratio of TiO₂ to Fe₃O₄ in the synthesized particles. There is an increase in the activity with an increase in the molar ratio of the TiO₂ and vice versa. The synthesized particles were effective in the reduction on phosphate, nitrate and dye removal at lower concentrations of targeted compound. The magnetic properties of the synthesized particles also decrease when the ratio of the TiO₂ increased. The results show that these particles have

very good photocatalytic activity for purifying wastewater. It can be concluded that the treatment process occurs at shorter time making it inexpensive.

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