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STABILITY ANALYSIS OF CARRIER OILS MEDIATED IRON OXIDE NANOPARTICLES AND ITS PHOTODEGRADATION STUDIES

K. L. PALANISAMY*, V. DEVABHARATHI[a] and
N. MEENAKSHI SUNDARAM[b]

Department of Physics, Sengunthar Engineering College, TIRUCHENGODE (T.N.) INDIA
[a]Department of Physics, KSR Institute for Engineering and Technology, TIRUCHENGODE (T.N.) INDIA
[b]Department of Biomedical Engineering, PSG College of Technology, COIMBATORE (T.N.) INDIA

ABSTRACT

Iron oxide nanoparticles (IONPs) were synthesized with olive oil and linseed oil as stabilizers by co-precipitation method. The dried nanoparticles were stored in a room at room temperature over a period of six months. The stability assessment was done by measuring poly dispersity index (PDI), zeta potential measurement, pH values and thermo gravimetric analysis (TGA). Further the photodegradation of Acridine Orange (AO) dye was taken for the better stability offered by olive oil stabilized IONPs using UV-visible spectrophotometer. Effect of pH and intensity of light on photocatalytic degradation of AO dye with olive oil stabilized IONPs were also analysed.

Key words: Iron oxide nanoparticles, Carrier oils, Stability, Photodegradation.

INTRODUCTION

Stability of IONPs

Magnetic iron oxide nanoparticles represent a fascinating material for various researchers due to their biomedical applications in the treatment of solid tumours[1] or contrast agents[2]. In order to be efficient in biological applications, colloidal suspensions of magnetic nanoparticles must have long time stability and the magnetic core must respond to an external magnetic field that directs the particle to a desired location. The nanoparticles stability is influenced by the size, structure and composition of the particle with a narrow

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*Author for correspondence; E-mail: klpalanisamy@gmail.com; Ph.: +9199651-39339,
Fax: 91-4288-255716

dimensional controlled polydispersity. These are the essential requirements for magnetic fluids to flow through the capillaries of diameter of 1.4 μm. The colloidal stability of magnetite particles is achieved by coating the magnetic core with a surfactant to have the particles to be dispersed in a carrier fluid.

The stability of the particles can be enhanced by coating with biocompatible surfactants[3] capable of interactions with hydroxyl groups on the magnetite surface and ensuring the ferrofluid stability. The coating agent should have specific functional groups for further functionalization for specific applications. Metals such as Fe, Co and Ni, which oxidize easily, are not recommended in biomedical uses due to the higher probability of oxidizing inside human bodies. This problem can be solved using magnetite particles that not only present a greater stability to oxidation, but can be coated with different specific surfactants, increasing their resistance to oxidation[4-6]. Hence, the making of magnetic IONPs nanoparticles with non toxic carrier oils such as olive oil and linseed oil has been carried out here to achieve better stability by adopting green synthesis as described in our previous studies.

Photocatalytic degradation of acridine orange (AO) dye

Industrial development on human life causes big environmental threats due to the continuous release of industrial pollutants, which create many serious problems because they are carcinogenic. Hence, it is a urgent need to save the environment by detoxification of these pollutants. Many physical, chemical, and biological methods were developed for water treatment but less beneficial obtained because of low efficiency, more cost and time consumption. Photocatalysis is a great boon in photodegradation of organic pollutants[7], has attracted much attention in recent years. Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons from the sunlight, Infrared radiation, visible light, and ultraviolet light are the regions of wavelengths cause the photodegradation process. Photodegradation includes photodissociation, the breakup of molecules into smaller pieces by photons. It also includes the change of a molecule's shape to make it irreversibly altered, such as the denaturing of proteins, and the addition of other atoms or molecules. A common photodegradation reaction is oxidation. This type of photodegradation is used by some drinking water and wastewater facilities to destroy pollutants.

Photodegradation of a dye is described as a colored material and which has an affinity to the substrate to which it is being applied. A pigment generally is insoluble, and has no affinity for the substrate. Iron oxide nanoparticles can be a better photocatalyst than the commonly used TiO_2 NPs due to its less band gap of 2.2 eV than the wide bandgap of

3.2 eV of TiO_2 NPs[8]. The better photocatalytic performance of IONPs than TiO_2 NPs can be recognized to considerable generation of electron–hole pairs through the narrow band-gap illumination[9]. The better separation between electrons and holes would allow a better efficiency for oxidation and reduction reactions[10], thus enhancing the photocatalytic activity.

Organic dyes such as Acridine Orange (AO) are the common pollutants and affect the environment due to its hazardous and carcinogenic nature. Acridine orange binding with the nucleic acid occurs in both living and dead bacteria, also other microorganisms. Acridine orange is useful for enumerating the microbes in a sample. The dye is often used in epifluorescence microscopy. Thus detoxification of these organic pollutants needs an urgent and effective process. Several methods have been used but photocatalytic degradation is one of the superlative and attractive substitutes for the degradation of these organic pollutants in waste water[11]. Therefore, olive oil stabilized IONPs have been proposed as a catalyst for the detoxification of organic dye in the presence of UV radiation.

EXPERIMENTAL

Materials and methods

The iron oxide nanoparticles synthesized using co-precipitation method using carrier oils such as olive oil and linseed oil as stabilizing agent[12,13] and surfactant as we reported in our previous study. The average particle sizes were 20 nm and exhibited superparamagnetic behaviour. Further to compare the stabilization of these carrier oils stabilized IONPs with bare IONPs, a uncoated sample of IONPs was also prepared. These dried nanoparticles were stored at room temperature for about six months. As synthesized the three distinguished nanoparticles (shown in Fig. 1) uncoated, olive oil and linseed oil stabilized IONPs were stored at room temperature for six months.

Fig. 1: Synthesized IONPs (A) Uncoated (B) Olive oil stabilzed and (C) Linseed oil stabilized

Polydispersity index, zeta potential (10) and pH were evaluated after 6 months. The binding tendency of these fatty acid rich stabilisers on IONPs is studied with uncoated IONPs by performing thermogravimetric analysis (TGA) of the nanoparticles[14].

A stock solution of AO dye of 1.0×10^{-3} M concentration was prepared by dissolving 0.365 g of AO in 1000 mL of doubly distilled water. The absorption maximum of the dye was determined with the help of a spectrophotometer (Lambda 950). Photocatalytic degradation of AO was studied by taking 50 mL reaction mixture which contains 2.0×10^{-5} M of AO and 0.05 g of IONPs of olive oil mediated. The reaction mixture was exposed to light. For irradiation purpose, 200 W tungsten lamp (Philips) was used. The intensity of light was measured by solar power meter (Tenmars Model TM 207). A water filter was used to cut off thermal radiation. The pH of the solution was measured by a digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of 0.1 N sodium hydroxide and 0.1 N hydrochloric acid solutions. To measure the degradation of dye, optical density was taken at regular time intervals. The degradation was investigated by measuring the absorbance using UV-visible spectrophotometer (Lambda 950).

RESULTS AND DISCUSSION

Stability assessment

After storing the iron oxide nanoparticles at room temperature over a period of six months, no significant changes were noted in mean diameter of the nanoparticles. This indicates that over this six months period, vegetable oil stabilized iron oxide nanoparticles remained physically stable. Thus the olive oil and linseed oil coated IONPs show better stability for the use of biomedical applications.

Table 1: Stability analysis : Initial physicochemical characteristics of nanoparticles

IONPs	PDI	Zeta potential (mV)	pH
Uncoated	0.27 ± 0.07	- 21.5	10.42
Olive oil coated	0.23 ± 0.04	-39.6	11.15
Linseed Oil coated	0.19 ± 0.02	-37.8	10.57

As it can be observed in Table 1 and 2, that after 6 months of storage uncoated, Olive oil and flaxseed oil coated IONPs showed a slight decrease in polydispersity indices and a significant decrease in pH values and zeta potential values compared to the initial characteristics. The pH value of bare IONPs is decreased as much the decrease in pH of the vegetable oil coated IONPs. It may be due to the hydrolysis or the relaxation of the triglyceride chains of the oils. i.e., the liberated free fatty acids were responsible for the reduction in the emulsion pH and zeta potential values.

Table 2: Stability analysis : Physicochemical characteristics of nanoparticles after six months storage at room temperature and protected from light

IONPs	PDI	Zeta potential (mV)	pH
Uncoated	0.26 ± 0.04	-19.2	7.84
Olive oil coated	0.18 ± 0.08	-37.4	4.26
Linseed oil coated	0.12 ± 0.04	-34.2	5.19

The zeta potentials of the nanoparticles were found to decrease slightly over a period of six months. Immediately after the preparation of the nanoaparticles, the measured zeta potential were about - 21.5 mV (Bare IONPs), - 39.6 (Olive oil coated IONPs) and -37.8 (Linseed oil coated IONPs) as shown in Table 1. The observed high negative zeta potential values of carrier oils stabilized IONPs were sufficient enough to prevent agglomeration by random collisions even at elevated temperature. Keeping the nanoparticles emulsion at room temperature for up to 6 months decreased the zeta potential to – 19.2 mV, – 37.4 mV and – 34.2 mV for uncoated, Olive oil, Linseed oil IONPs, respectively. In addition to the decrease in pH values of these formulations, these also presented a significant increase in their potential zeta values, which was due to the presence of free fatty acids on the particle surface of, Olive oil and Linseed oil stabilized IONPs as shown in Fig. 2.

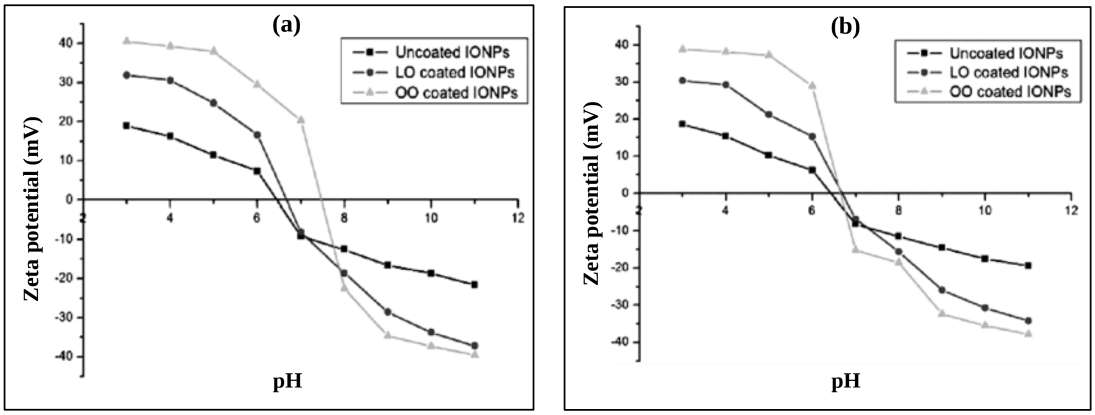

Fig. 2: Zeta potential of IONPs (a) during synthesis (b) after six months

These two oils with high amounts of oleic and α-linoleic acids and other unsaturated fatty acids, which could undergo oxidative and hydrolytic reactions in contact with aqueous medium and temperature below 100°C, forming free fatty acids. The occurrence of oxidative/hydrolytic reactions during the storage time was confirmed by the development of a characteristic odour in all formulations after 6 months of storage.

Thermogravimetric analysis (TGA)

Fig. 3 shows that the comparison of three samples obtained, where uncoated IONPs exhibit total mass loss of 13.5% at temperature exceeding 350°C and the other two samples (Olive Oil stabilized and Linseed Oil stabilized IONPs) exhibit a total mass loss about 10% and 11%, respectively with however some differences in the decomposition behaviour at lower temperatures. This result predicts that the vegetable oil coated IONPs show better stability than the uncoated IONPs.

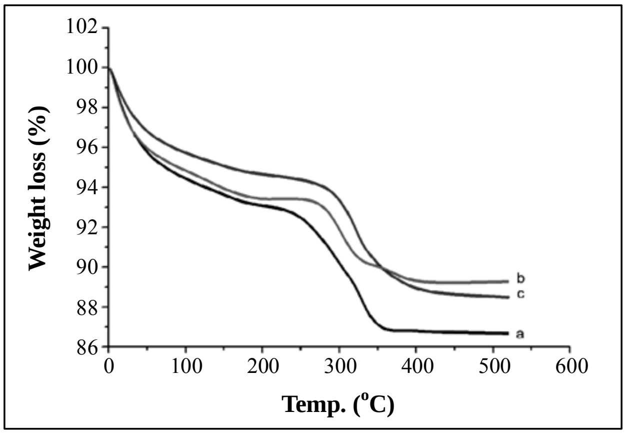

Fig. 3: TGA of IONPs (a) Uncoated (b) Olive oil stabilized (c) Linseed oil stabilized

Photodegradation activity

The molecular structure and absorbance spectra of AO are presented in the below Figs. 4 and 5, respectively. The photodegradation of the AO dye occurs predominantly on the olive oil stabilized IONPs surface. The extent of degradation of the AO dye was measured by monitoring its concentration with and without IONPs after reaching the degradation. It is observed that the irradiation of an aqueous suspension of AO dye in the presence of iron oxide NP leads to decrease in absorption spectra at 491 nm.

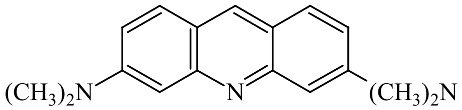

Fig. 4: Molecular structure of AO

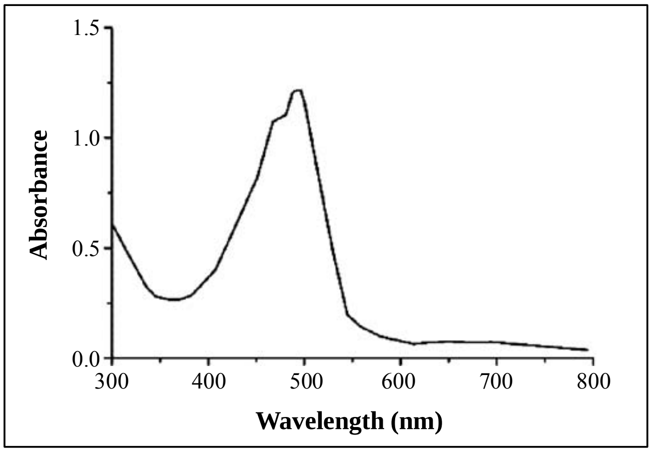

Fig. 5: Spectrum of aqueous solution of AO

The absorbance spectra at 491 nm is drastically decreased with increasing in exposure time and gradually decrease until 150 min, which concludes that the AO dye has de-colorization property with iron oxide NPs close to 65%. The decrease in absorption intensity against irradiation time for the AO in the presence and absence of olive oil stabilized IONPs is shown in the Fig. 6. Fig. 7 shows the plot for the percent degradation versus irradiation time (min) for the oxygen saturated aqueous suspension of AO in the presence and absence of Olive oil stabilized IONPs. It shows that around 40% degradation of the AO dye takes place after 150 min of irradiation in the presence of Olive oil stabilized IONPs.

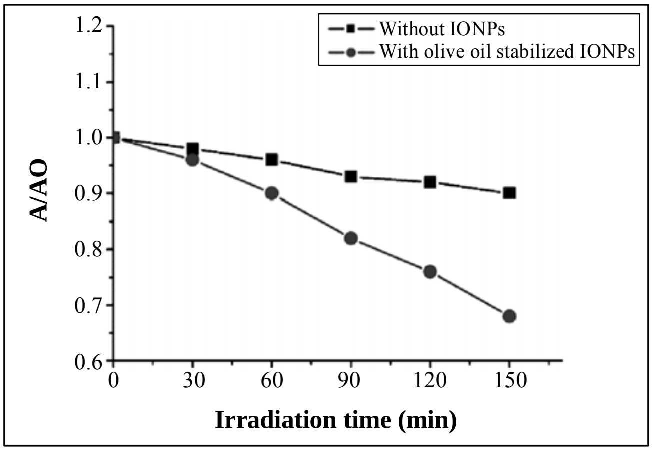

Fig. 6: Photocatalytic degradation of AO using iron oxide NPs : Change in absorbance with and without olive oil stabilized iron oxide NPs

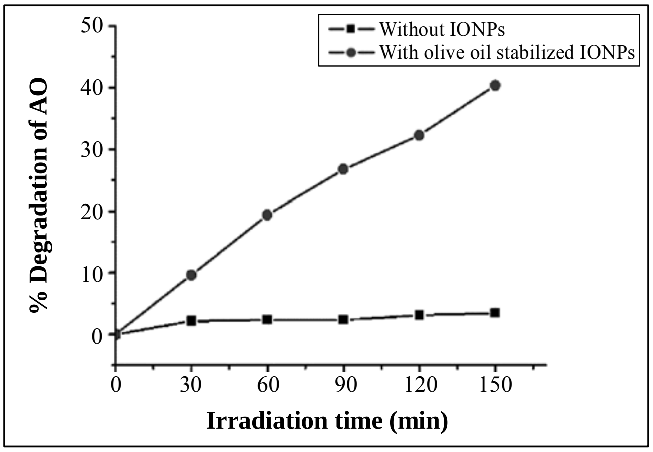

Fig. 7: Photocatalytic degradation of AO using olive oil stabilized IONPs : Percentage of degradation in different time intervals of AO in presence and absence of iron olive oil stabilized IONPs

The experimental degradation rate constant is obtained from the initial slope acquired by linear regression from a plot of the natural logarithm (ln) of absorbance of the AO as a function of exposure time, i.e., first-order degradation kinetics. This rate constant is used to evaluate the degradation rates for the decomposition of AO by using the formula.

$$-\frac{d(A)}{dt} = kcn$$

Where, *k* is the rate constant, c is the concentration of the pollutant, and n is the order of reaction.

Table 3: Photodegradation study of AO dye using olive oil stabilized IONPs

Time (min.)	Optical density (O.D)	2 + log O.D
0	1.181	2.072
30	0.677	1.831
60	0.421	1.625
90	0.245	1.390
120	0.152	1.182
150	0.086	0.934

It was observed that the absorbance of the solution decreases with increasing time intervals showing thereby that the concentration of the dye decreases with increasing time of exposure. A plot of 2 + log O.D. versus exposure time, as shown in Fig. 8, was linear and follows first order kinetics. The rate constant was determined by using the expression, k = 2.303 × slope.

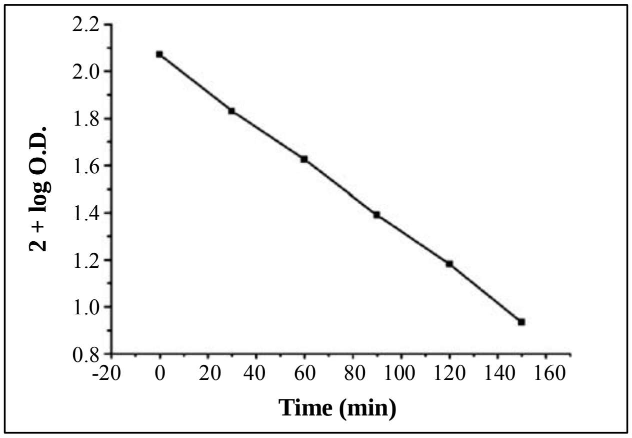

Fig. 8: Exposure time Vs 2 + log O.D.

Effect of pH on photocatalytic degradation of dye

The pH of the prepared solution is probably affecting the degradation of dye and hence, the effect of pH on the rate of degradation of the dye was investigated in the pH range 6 to 10. The results were reported in Table 4. It has been observed that the rate of reaction increased with increasing pH of the solution upto pH 8.5. However, a further increase in pH of solution resulted in decreased reaction rate (Fig. 9).

Table 4: Effect of pH on degradation of AO

pH	k x 10^4 (sec^{-1})
6	0.27
6.5	0.43
7	0.74
7.5	1.59
8.0	2.69

Cont…

pH	k x 10^4 (sec^{-1})
8.5	3.56
9.0	2.54
9.5	1.64
10.0	0.94

An increase in the rate of photocatalytic degradation of acridine orange with increase in pH may be due to generation of more OH radicals, which are produced from the reaction between –OH ions and hole (h^+) of the semiconductor. Above pH 8.5, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of AO converts in its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to absorption of –OH ions.

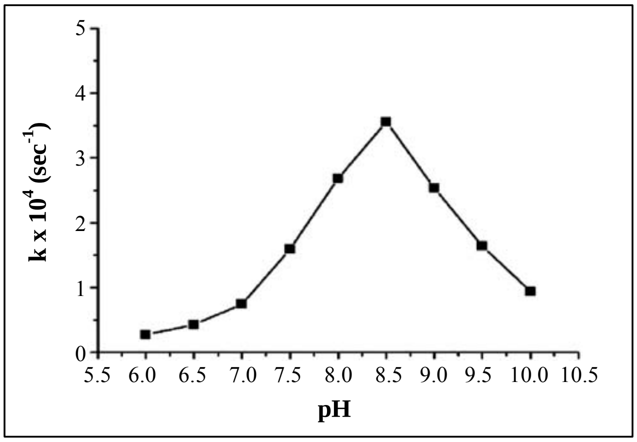

Fig. 9: Effect of pH on degradation of AO

Effect of light intensity on photocatalytic degradation of dye

The effect of intensity of the light on the rate of the reaction was also observed and the observations are summarized in Table 5 and it is plotted as shown in Fig. 10.

As observed, the increase in the intensity of light upto 600 Wm^{-2}, the rate of reaction also increases because on increasing the intensity, the number of photons striking per unit area of reaction mixture will also increase. This will result in a corresponding increase in the rate of degradation of AO dye. Small decrease in the rate on further increasing light intensity may be due to some thermal or side reactions.

Table 5: Effect of light intensity on degradation of AO

Light intensity (W/m^2)	k x 10^4 (sec^{-1})
200	1.92
300	2.08
400	2.59
500	3.76
600	4.14
700	3.14
800	2.43

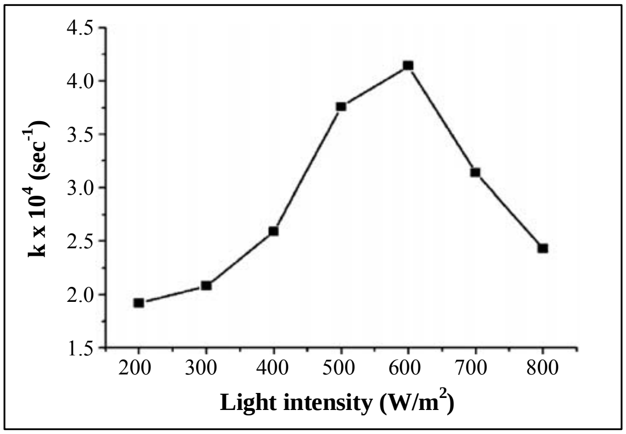

Fig. 10: Effect of light intensity on degradation of AO

CONCLUSION

This study showed for the feasibility to prepare nanoparticles using carrier oils as stabilizing agents. Nanoparticles prepared with these oils offered nanometric size range and negative zeta potential. The parameters evaluated such as PDI, Zeta potential and TGA have been adequate for better stability after 6 months of storage at room temperature, although a decline of pH was observed for all three IONPs. The photodegradation of AO clearly demonstrated that olive oil stabilized iron oxide NPs hold significant photocatalytic activity and these NPs could be beneficial photocatalysts for the removal of colored dyes. Results indicate that olive oil stabilized iron oxide NPs can be employed for the degradation of acridine orange dye with the variation of pH of the reaction mixture and intensity of light.

From the above results, it has been clearly indicated that the olive oil stabilized IONPs shows a good photocatalytic activity, thus it can be used as a photocatalyst for degradation of the synthetically prepared effluents and industrial effluent in waste water under illumination of UV light in the photoreactor.

REFERENCES

1. Gómez-Lopera, A. Salvador, J. L. Arias, V. Gallardo and Á. V. Delgado, Colloidal Stability of Magnetite/poly (Lactic Acid) Core/shell Nanoparticles, Langmuir, **22(6)**, 2816-2821 (2006).
2. Stark, D. David, Ralph Weissleder, Guillermo Elizondo, P. F. Hahn, S. Saini, L. E. Todd, J. Wittenberg and J. T. Ferrucci, Superparamagnetic Iron Oxide: Clinical Application as a Contrast Agent for MR Imaging of the Liver, Radiology, **168(2)**, 297-301 (1988).
3. S. Jing, S. Zhou, P. Hou, Y. Yang, J. Weng, X. Li and M. Li, Synthesis and Characterization of Biocompatible Fe_3O_4 Nanoparticles, J. Biomed. Mater. Res. Part A, **80(2)**, 333-341 (2007).
4. L. Sophie, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst and R. N. Muller, Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications, Chemical Reviews, **108(6)**, 2064-2110 (2008).
5. Ajay Kumar Gupta and Mona Gupta, Synthesis and Surface Engineering of Iron Oxide Nanoparticles for Biomedical Applications, Biomaterials, **26(18)**, 3995-4021 (2005).
6. W. Wei, Q. He and C. Jiang, Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies, ChemInform, **40(24)** (2009).
7. O. Akhavan and R. Azimirad, Photocatalytic Property of Fe_2O_3 Nanograin Chains Coated by TiO_2 Nanolayer in Visible Light Irradiation, Appl. Cataly. A: General, **369(1)**, 77-82 (2009).
8. J. Bandara, J. A. Mielczarski, A. Lopez and J. Kiwi, Sensitized Degradation of Chlorophenols on Iron Oxides Induced by Visible Light: Comparison with Titanium Oxide, Appl. Cataly. B: Environ., **34(4)**, 321-333 (2001).
9. L. Guo-guang, Xue-Zhi Zhang, Ya-Jie Xu, Xin-Shu Niu, Li-Qing Zheng and Xue-Jun Ding, Effect of $ZnFe_2O_4$ Doping on the Photocatalytic Activity of TiO_2, Chemosphere, **55(9)**, 1287-1291 (2004).

10. X. Piao, G. Ming Zeng, D. Lian Huang, C. Ling Feng, S. Hu, M. Hua Zhao and C. Lai, Use of Iron Oxide nanomaterials in wastewater treatment: A Review, Science of the Total Environ., **424**, 1-10 (2012).
11. K. L. Palanisamy, N. Meenakshi Sundaram, V. Devabharathi and P. Thangarasu, Synthesis and Characterization of Olive Oil Mediated Iron Oxide Nanoparticles, Digest J. Nanomater. Biostr., **8(2)**, 607-612 (2013).
12. K. L. Palanisamy, V. Devabharathi and N. M. Sundaram, The Utility of Magnetic Iron Oxide Nanoparticles Stabilized by Carrier Oils in Removal of Heavy Metals from Waste Water, Int. J. Res. Appl., Nat. Soc. Sci., **1(4)**, 15-22 (2013).
13. M. Nidhin, R. Indumathy, K. J. Sreeram and B. U. Nair, Synthesis of Iron Oxide Nanoparticles of Narrow Size Distribution on Polysaccharide Templates, Bull. Mater. Sci., **31(1)**, 93-96 (2008).
14. M. Sou-Yee and Dong-Hwang Chen, Fast Adsorption of Methylene Blue on Polyacrylic Acid-bound Iron Oxide Magnetic Nanoparticles, Dyes and Pigments, **61(1)**, 93-98 (2004).

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