Vol. 4 Iss. 2 (2015)
BLPN 201504-01-00046

Journal of Biological and Information Sciences
ISSN: 2320-1290

Research article

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Green synthesis of iron nanoparticles and investigation of their effect on degradation of dyes

Received 13 April 2014; accepted 16 April 2015; published online 30 April 2015

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Abstract

The work involves the synthesis of magnetic nanoparticles (MgNPs) using chemical (co-precipitation method) and biological method in order to provide a comparative analysis of the efficiency of different synthesising techniques. The ability of the MgNPs to photocatalytically degrade the Methyl Orange dye was optimised in different conditions, such as darkness, UV light, artificial light and sunlight. As a result, it was discovered that biologically synthesised MgNPs under the influence of sunlight were able to degrade 0.99% of the dye; whereas, the chemically synthesised MgNPs were unable to do the same. This method of degradation of dyes can be implemented for control and degradation of dyes at various industries like textile, colour, food industries, etc.

Keywords

Magnetic nanoparticles; Dye degradation; Methyl Orange; Iron nanoparticles; Photocatalytic; Biological synthesis

Introduction

In recent times, sources of dye contamination have expanded from textile industries to food, paper, printing, cosmetic and pharmaceutical companies.[1] When these dyes are not treated properly they get accumulated in the environment and become a threat to the ecosystem. Since the dyes are chemically and photolytically stable, they maintain the same colour for a longer period of time in the natural environment.[2,3] Hence, these non treated dyes are potentially carcinogenic, mutagenic and genotoxic. The example of such dyes include Acid Red 26, Direct Blue 6, Direct Black 38, Direct Red 28, Basic Red 9, Basic Violet 14, Disperse Blue 1, Disperse Orange 11 and Disperse Yellow 3.[4] Consequently, the release of potentially hazardous dyes in the environment can be an eco-toxic risk and can also affect humans through the food chain.[2,3]

Conventional chemical and physical dye degradation techniques are either expensive, highly time consuming, result in sludge formation, or result in the formation of by-product.[5] The extraordinary properties possessed by nanoparticles make dye degradation more effective than conventional methods of dye degradation. These particles have high surface to volume ratio and high fraction of surface atoms. At nano level, they have specific physicochemical properties, such as optical, magnetic and catalytic properties. Nanoparticles have been successfully used in the past for the degradation of dyes, e.g. CdS nanoparticles for Methylene Blue degradation,[6] TiO_2 nanoparticles for visible light induced degradation of a textile diazo dye, Naphthol Blue Black,[7] Manganese-doped ZnO nanoparticles for photocatalytic degradation of organic dyes,[8] Zinc Ferrite nanoparticles for Reactive Red 198 (RR 198) and Reactive Red 120 (RR 120) degradation,[9] Iron Oxide nanoparticles for the degradation of azo dye Orange II[10] and Reactive Red 120 in aqueous solutions using homogeneous/heterogeneous iron systems,[11] and Fe_2O_3 nanoparticles for photocatalytic degradation of Methyl Orange.[12]

Currently, nanostructured magnetic materials with hetero junction arrangement have been extensively applied to photocatalysis.[13] On large scale, these nanoparticles have been produced chemically which is not an eco-friendly approach. Thus, a non-toxic, cost-effective and eco-friendly route for synthesis of nanoparticles is required.[6] In this article, we report the optimised condition for the degradation of dye, Methyl Orange using chemically and biologically reduced magnetic nanoparticles. Magnetic nanoparticles possess high photocatalytic activity for dye degradation, no dissolution of nanoparticles during degradation, high magnetization for easy magnetic separation, etc.[3] These properties make them a suitable candidate for the degradation of dyes. In the biological approach, green tea extract has been taken as the reducing and capping agent.[14] Polyphenols present in green tea, such as flavonoids have anti-oxidants that are very good reducing agent and have the ability to form complexes with metal ions. Furthermore, higher contents of proteins, lipids and amino acids also constrain agglomeration by stabilising the growth of nanoparticles.[15]

Materials and Methods

Chemicals

Ferric chloride salt, ammonia, Methyl Orange and other chemicals used in the research work have been procured from Merck India.

Method of synthesis of magnetic nanoparticles

Chemical synthesis

For the synthesis of magnetic nanoparticles through co-precipitation method, 3.7 g of ferric chloride and 9.54 g of ferrous sulphate were mixed separately in 500 ml of distilled water.

Thereafter, in a 1000 ml Erlenmeyer's flask both solutions were added and stirred at 80°C for 10 min. After mixing, 20 ml of ammonia was added and the change in colour from orange to black was visibly observed.[16]

Biological synthesis

For the synthesis of magnetic nanoparticles through co-precipitation method using green tea extract as reducing and capping agent, 3.7 g of ferric chloride and 9.54 g of ferrous sulphate were mixed separately in 500 ml of distilled water.

Thereafter, in a 1000 ml Erlenmeyer's flask both solutions were added and stirred at 80°C for 10 min. After mixing, 25 ml of freshly prepared green tea extract was added followed by 20 ml ammonia after a period of time. Change in colour from orange to black was visibly observed confirming the formation of black magnetic nanoparticles.[17]

Purification

For the removal of excess of ammonia from magnetic nanoparticles, the particles were washed thoroughly with distilled water thrice by discarding the supernatant, followed by ethanol wash, and dried in hot air oven for 45 min.[13]

Standardisation for the degradation of dye

For the optimisation of dye concentration and magnetic nanoparticles concentration, following measures were taken. First, the concentration of magnetic nanoparticles was fixed and the concentration of dye was varied. Then, the concentration of magnetic nanoparticles was varied and the concentration of dye was fixed. For the optimisation of dye concentration, different stock concentrations were maintained, such as 2 mg/100 ml, 4 mg/100 ml and 6 mg/100 ml. The percentage of dye degradation was estimated by the following formula[18]:

$$\%\ of\ Degradation = \left(\frac{C - C'}{C}\right) X\ 100$$

Where,
C - is the initial concentration of dye solution and
C' - is the concentration of dye solution after photocatalytic degradation

Environmental effects on dye degradation

Samples with identical amount of magnetic nanoparticles and dye concentration were kept in different physical environment to study the effect of environmental conditions on dye degradation.

Different physical conditions under which the optimisation of dye degradation was studied included darkness, artificial light, UV light and sunlight.

Results and Discussion

Green tea extract acts as a reducing and capping agent as a result of the presence of polyphenols.[14] Due to this, the biological synthesis of magnetic nanoparticles has higher yield in comparison to chemical approach.

After performing the degradation under various different environmental conditions, it can be inferred from Fig. 1 that sunlight when coupled with biologically synthesised magnetic nanoparticles has the ability to degrade the dye more than other conditions. Studies show that, sunlight assists in the degradation of dye[19] and that iron doped or functionalised nanoparticles show excellent photocatalytic activity under visible light than non-functionalised or un-doped nanoparticles.[20,21] To increase the efficiency of the dye degradation process, nanoparticles functionalised with citric acid,[3] hydrogen peroxide[19] and activated carbon[22] have also been used in various studies.

Table 1. UV spectroscopy values for Methyl Orange degradation using biologically synthesised nanoparticles at 464 nm

NPs conc.	Dye conc.		
	2 mg/100 ml	4 mg/100 ml	6 mg/100 ml
0 mg	0.509	0.568	0.793
20 mg	0.504	0.567	0.847
40 mg	0.558	0.660	0.881
60 mg	0.660	0.764	1.046

Table 2. UV spectroscopy values for Methyl Orange degradation using chemically synthesised nanoparticles at 464 nm

NPs conc.	Dye conc.		
	2 mg/100 ml	4 mg/100 ml	6 mg/100 ml
0 mg	0.177	1.080	1.223
20 mg	0.370	0.691	1.41
40 mg	0.439	-	-
60 mg	0.773	1.159	-

'-' = Values exceeding UV range

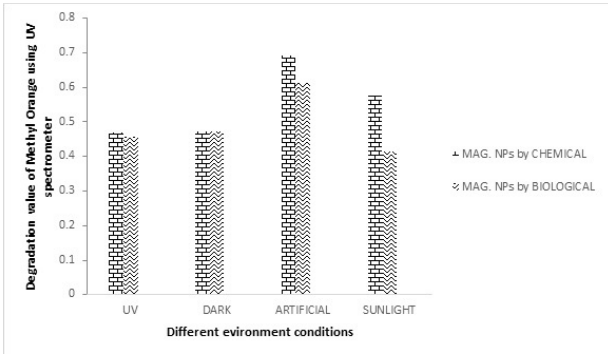

Fig. 1. Degradation of dye under different environmental conditions

Furthermore, from Fig. 1 it can be inferred that in different environmental conditions biologically synthesised magnetic nanoparticles show much better performance in degrading the dye than chemically synthesised magnetic nanoparticles. Iron-polyphenol nanoparticles behave as Fenton like catalysts for discolouration of azo dyes. [23]

Here, magnetic nanoparticles capped with green tea's polyphenols are responsible for degrading the dye better than chemical method. From Table 1 and 2, it can be observed that the appropriate concentration of dye at which maximum degradation can take place is 2 mg/100 ml or lesser.

As the concentration of the dye increases, the amount of dye adsorbed per molecule of the nanoparticle increases, the path length of the photons entering the solution decreases and the rate of dye degradation also decreases, and this affects the active sites of the nanoparticles and thereby decreases the efficiency of the nanoparticles.[24,25]

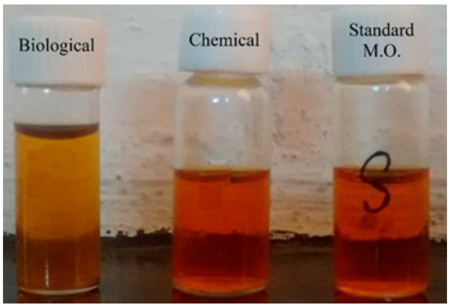

Fig. 2. Degradation of dye can be visibly seen as change in colour from dark to light after the treatment with biological and chemically synthesised magnetic nanoparticles

Conclusion

The studied research has shown that, biological synthesis of magnetic nanoparticles is easy, rapid and cost-effective method for the synthesis of nanoparticles. Furthermore, it was proved that they were more effective in degrading Methyl Orange dye than chemically synthesised magnetic nanoparticles. The study of dye degradation in different environmental conditions evidenced that, under the influence of sunlight the degradation activity is more than the degradation activity found in artificial, UV and dark environments. As a result, it was discovered that biologically synthesised MgNPs under the influence of sunlight were able to degrade 0.99% of the Methyl Orange dye. Whereas, it was found that chemically synthesised MgNPs were unable to do the same. The above study can be put to use effortlessly because it only requires sunlight and biologically synthesised magnetic nanoparticles in order to degrade the dye present in the stagnated water. Reducing agents can be used in order to increase the efficiency of dye degradation process. Hence, no industrial set up is required for the above process to take place. This research can be implemented in the degradation of the dyes released by textile industries, food industries, pharmaceutical industries and cosmetic industries where untreated dye water is discharged in excess.

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