GREEN SYNTHESIS OF PHOTOCATALYST FOR DEGRADATION OF DYES.

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Abstract

Release of dyes into the environment has created a major global concern. Congo red, an anionic diazo dye is toxic to organisms and its presence in water is highly visible and undesirable. These study aim at investigating the applicability of green synthesized iron nanoparticles (Fe NPs) as a Fenton-like catalyst in the photocatalytic degradation of dye effluents. Fe NPs were synthesized using extract of mango leaves.Characterization of the material with SEM and FT-IR showed that the material mainly comprises of iron oxide and iron oxohydroxide. Congo red and malachite green were degraded with the Fe NPs using the photodegradation method. The obtained iron nanoparticle were also utilized as a Fenton – like catalyst which aided degradation of the dye using H_20_2. The degradation of the dye in aqeous solution were monitored with ultraviolet visible spectroscopy. Result indicated the degradation of both effluents on exposure to sunlight over time and an accelerated degradation of both dyes in presence of Fenton catalyst. It is concluded that these eco – friendly method of degradation can find application in the control and degradation of dyes at various industries such as food and textiles.

Keywords: Congo red, Fenton catalyst, Photocatalytic degradation

Introduction

Water is a vital requirement of life. It is used for various household as well as industrial activities. It is one of the most essential natural resources, unfortunately exploited the most. The key reason being increased human population, rapid industrialization, increased living standard and urbanization. Rapid urbanization of natural resources, like increase in industries, especially textile industries is posing a threat to the water bodies as these discharge effluents with various harmful and toxic components, mainly dyes. This deteriorates the quality as well as quantity of water and makes it unsafe for further use (Gupta *et al.,* 2015).

It has been estimated that the total dye consumption in textile industry worldwide is more than 10,000 tons per year and about 10–15% of these dyes are released as effluents during the dyeing processes (Gupta *et al*., 2013). Synthetic dyes are of great environmental concern due to their widespread usage and their low removal rate during aerobic waste treatment. About 10,000 different dyes are prepared globally and approximately 8×105 tons of synthetic dyes is consumed in textile industries in the whole world (Walker and Weatherley, 1997). In Textile industries 93% of the intake water comes out as colored wastewater due to dyes containing high concentration of organic compounds and heavy metals (Wijannarong *et al.,* 2013; Gupta *et al*., 2014). The non- biodegradable nature of the dyes in the spent dye baths of textile industries constitutes a serious environmental hazard. The color of wastewater is aesthetically unpleasant to aquatic bodies which hinder the oxygenation ability of water, disturbing the whole of the aquatic ecosystem (Xu *et al*., 2005) and food chain. Approximately 10,000 different dyes and pigments are produced worldwide and used extensively in the dye and printing industries. These dyes are considered to be recalcitrant, and toxic. Dyes are difficult to degrade biologically, so that degradation of dyes has received considerable attention. About 10-15% of all dyes are directly lost to wastewater in the dyeing process (Anbia and Ghaffari, 2011). Thus, the wastewater must be treated before releasing into the natural environment. They resist microbial biodegradation and are therefore not easily degraded in wastewater treatment plant (Maithri *et al*., 2014). Textile effluents comprise of different dyes hence it becomes essential to promote the prevailing techniques as well as to look for new techniques that decolorize the mixture of dyes rather than a single dye solution.

Conventional waste water treatment methods like adsorption, ultra-filtration, chemical and electrochemical methods (Tang *et al*., 1995) are not efficient to remove recalcitrant dyestuffs

(a)

(b)

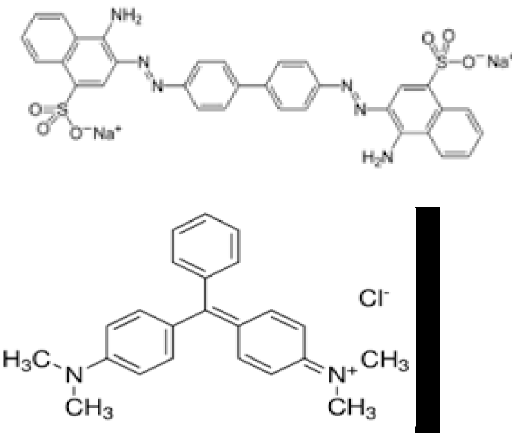

Figure 1: Structure of (a) Congo red Dye (b) Malachite green dye

from effluents. Several physical and chemical methods are effective but have high operating costs and limited applicability (Gupta and Manisha, 2012). Thus, treatment of dye is yet, one of the challenging tasks in environmental field. Currently available methods such as chemical oxidation, reverse osmosis, adsorption, etc., suffer from disadvantages such as high cost, regeneration problems and secondary pollutants/sludge generation.

The superiority of photo-catalytic degradation by nanoparticles in wastewater treatment is due to its advantages over the conventional methods, such as quick oxidation, no formation of polycyclic products and oxidation of pollutants. It is an effective and rapid technique in the removal of pollutants from wastewater (Sobana *et al*., 2006). In the recent years, numerous metal oxides including TiO_2 (El-kemary *et al*., 2011), ZnO (Ullahs *et al*., 2008), and other oxides have attracted growing attentions for photo-degradation of organic dyes.

Nanoscale iron nanoparticles are recently gaining interest in nanoscale remediation circles (Uzum et al., 2008). Iron nanoparticles containing iron oxide and zerovalent iron (ZVI) can be used as a fenton-like catalyst for the degradation of aqeous organic solutes (Xu and Wang, 2011). Due to the nanoscale size, high surface area and high surface reactivity can be obtained. Synthesis of iron oxide nanoparticles via a green synthetic route is an evolving method that would impact steric stabilization of iron nanoparticles against aggregation and also help to overcome corrosiveness and flammability in routine synthesis that have been reported (Hoag *et al*., 2009). The Fenton process is based on the action of hydroxyl radical (OH•) generated in aqueous solution by the well known Fenton reagent which is a combination of Fe^{2+} and H_2O_2, in aqueous solution (Byung-Hyun *et al*., 2011). Iron oxides, iron oxohydroxide, and zerovalent iron can be used as a source of ferrous ions in a Fenton-like process (Shahwan *et al.,* 2011). The sorption rate could be a controlling factor of the whole catalytic oxidation reaction (Shahwan *et al*., 2011). Therefore, the surface area and surface activity of Fenton catalyst is important. Recent report indicates the successful synthesis of iron nanoparticles using green tea leaves and sorghum bran extract (Njagi *et al*., 2009)

In this current research, synthesis of iron nanoparticles were carried out using mango leaves. Mango leaves are known to contain polyphenols which acts as a reducing and capping agent. The main objective of the current research work is to investigate the ability of a mango leaf synthesized iron oxide nanoparticles as a fenton catalyst in the degradation of malachite green dye and congo red dye. Another objective is to compare the extent of degradation of the dyes using H_2O_2 and without H_2O_2. The oxidative decolorization over a wide range of period of contact was then studied using UV-Visible spectrophotometer.

2 **Materials and Method**

2.1 Sample collection

Hydrated Iron II chloride ($FeCl_2.4H_20$), Iron (III) chloride ($FeCl_3$), Malachite green and Congo red were obtained from Kem Light Laboratory Limited, Ile Ife, Nigeria. Mango leaves were plucked from a mango tree within the surrounding of Chemistry Department, Obafemi Awolowo University, Ife Nigeria. Hydrogen peroxide (30% W/V) solution was purchased from SD Fine Chemical Limited. All other reagents used in this study were of analytical grade and are used without any further purification.

2.2 Extraction of Polyphenol in Mango leaves

Preparation of polyphenol which acted as the reducing and capping agent in the degradation of dye was synthesized from mango leaves. The mango leaves were handpicked from the mango tree into a clean bowl, washed, air dried for about 20 minutes and squeezed with deionized water until the green colored solution was obtained. The solution was sieved with Buckner funnel to obtain a particle free solution of polyphenol. 200ml of the solution was transferred into $1000cm^3$ round bottom flask and made up to mark with deionized water and kept for further use.

2.3 Preparation of Reagents

2.3.1 Preparation of hydrated iron (II) chloride ($FeCl_2.4H_2O$) solution and Iron (III) chloride ($FeCl_3$) solution

0.2g of $FeCl_2.4H_2O$ and $FeCl_3$ was weighed and dissolved with deionized water. The mixture was transferred into a $1000cm^3$ round bottom flask and made up to mark with deionized water.

2.3.2 Preparation of Hydrogen Peroxide (H_2O_2) solution

Hydrogen peroxide (30% w/v) having molecular weight of 34.01g/mol; it implies that 100ml of the solution contain 30g. Hence, 10ml of hydrogen peroxide is added to each solution of the dyes.

2.4 Preparation of Congo red and malachite green dye solution

A solution of each dye was prepared by weighing 0.02g differently into a beaker. The dyes were dissolved with deionized water and the solution was transferred into a $1000cm^3$ round bottom flask. The dye solution obtained was covered with aluminum foil to avoid degradation from the laboratory fluorescent light.

2.5 Green Synthesis of Iron Nanoparticles (FeNPs)

40ml of the plant extract and 100ml of FeNPs were measured, respectively. The solution were mixed together and heated at 60^0C for 30mins. The solution was left to stand for 10 minutes. Afterwards, an upper layer of clear solution and a lower layer of black residue were observed. The black residue at the lower layer indicated the formation of iron nanoparticles. The upper layer was decanted leaving behind the FeNPs which were then centrifuged for better settling.

2.6 Degradation Experiment

2.6.1 Degradation of Congo red dye with Iron nanoparticles without the addition of hydrogen peroxide.

100ml of iron nanoparticles solution were measured into a beaker; 40ml of the plant extract was added followed by the addition of 20ml of Congo red dye. The resulting solution obtained was placed under the sunlight for photo degradation to take place. After a time interval of 5, 10, 15, 20, 25, 30, and 60 minutes, 10ml of dye solution was taken respectively for UV analysis.

2.6.2 Degradation of malachite green and Congo red dye with FeNPs and hydrogen peroxide

Accurately, 100ml of FeNPs was measured respectively into two different beakers respectively. 40ml of the plant (mango leave) extract was added, followed by the addition of 20ml of the malachite green and 10ml of hydrogen peroxide solution. Same procedure was repeated for congo red dye. The resulting solution obtained was placed under sunlight for the photo degradation to take place. After a time interval of 5, 10, 15, 20, 25, 30, and 60 minutes, 10ml of dye solution was taken respectively for UV analysis.

2.6.3 Degradation of malachite green and Congo red dye with Fe^{3+} and hydrogen peroxide

Approximately, 200ml of Fe^{3+} was weighed into a beaker, and 40ml of the plant extract was added, followed by the addition of 20ml of malachite green dye and congo red into their respective beakers. 10ml of hydrogen peroxide and the resulting solution was placed under sunlight. After a time interval of 5, 10, 15, 20, 25, 30, and 60 minutes, 10ml of dye solution was taken respectively for UV analysis.

3 RESULTS AND DISCUSSION

3.1 Green synthesis of iron nanoparticles (Fe NPs)

The green synthesis of iron nanoparticles generated a black residue of non-aggregated iron nanoparticles which also take part as a reducing agent in the degradation of dye effluent. This can be related to the study of Njagi *et al.* (2011) that green synthesis of iron nanoparticles is evolving as a method that would impart steric stabilization of iron nanoparticles against aggregation, and help overcome the concerns related with using sodium borohydride as a reducing agent in routine synthesis reported so far. The synthesis of nanoparticles using plant extract is advantageous over microorganisms by eliminating the elaborate process of maintaining microbial culture (Ahmad *et al.,* 2003).

3.2 Malachite green and Congo red degradation experiment

3.2.1 Fenton-like mechanism

Degradation of pollutants from contaminated water can be achieved by chemical oxidation of organic molecules (Shaiwan et al, 2011). The oxidation is based on the action of hydroxyl radical (OH*), generated in aqeous solution by the well known fenton reagent (a combination of Fe^{2+} and hydrogen peroxide in aqeous solution (Moon *et al*., 2011). In the traditional fenton process, dissolved iron is used to replace a solid iron mineral (Xue *et al*., 2009), but the traditional fenton process has the disadvantage of producing large amount of sludge and the formation of a high concentration of the anions in the treated waste water (Moon *et al*., 2009). Unlike the traditional fentons reagent where the pH values have to be lowered below 4, the reaction between iron mineral and hydrogen peroxide oxidize the organic molecule at a neutral pH (Xue *et al*., 2009).

The general cycle of hydroxyl radical in a classical fenton system can be represented as

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{*} + OH^{-} \quad \text{------------ (i)}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + OOH^{*} + H^{+} \quad \text{------------ (ii)}$$

Both equations explains the initiation of the reaction by ferrous ions leading to production of hydroxyl radical which then attack the organic pollutants, hence, degrade them. These radical function by attacking bonds in the dye molecules, which might be in solution od adsorbed on the surface of the catalyst (Xue *et al*., 2009),. This can be related to azo dyes with an azo group. The cleavage of the azo bond in the chromophore of the dye leads to decolorization of the dye (Moon *et al*., 2011). Also, the nanosize of the mango leaf synthesized Fe NPs would doubtlessly increase its activity as a fenton-like catalyst (Kallel *et al*., 2009).

3.2.2 Degradation and Decolorization study

The changes in intensity of malachite green and congo red with time was analysed with UV-Visible Spectrophotometer. This is shown in figure 2-5. In figure 2 and 3, degradation is carried out in the absence and presence of the fenton catalyst respectively. From the spectra in fig 2, it was observed that there was no significance reduction in absorbance as exposure time increases. Here, little or no dye removal was achieved. From the absorption spectra in figure 3, dye removal proceeds almost immediately. A decrease in absorbance was observed as time increases. After 25 mins, almost 50% decolorization was achieved. In figure 3, there is presence of a catalyst (hydrogen peroxide) which generates hydroxyl radicals responsible for the breakdown of the molecules present in the dye effluent. This is confirmed from the work of Moon *et al.* (2011) that chemical oxidation of organic molecules is a powerful method for the degradation of pollutants from contaminated water. The oxidation is based on the action of hydroxyl radical generated in aqueous solution by the well-known Fenton reagent which is a combination of ferrous iron and hydrogen peroxide, in aqueous solution.

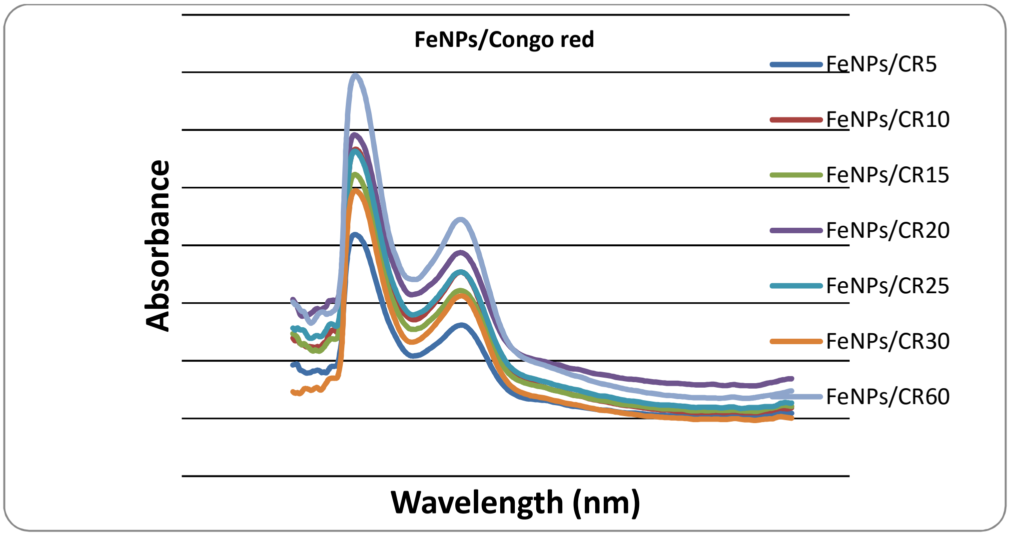

Figure 2; Absorption spectra showing degradation of CR by FeNPs under the visible light.

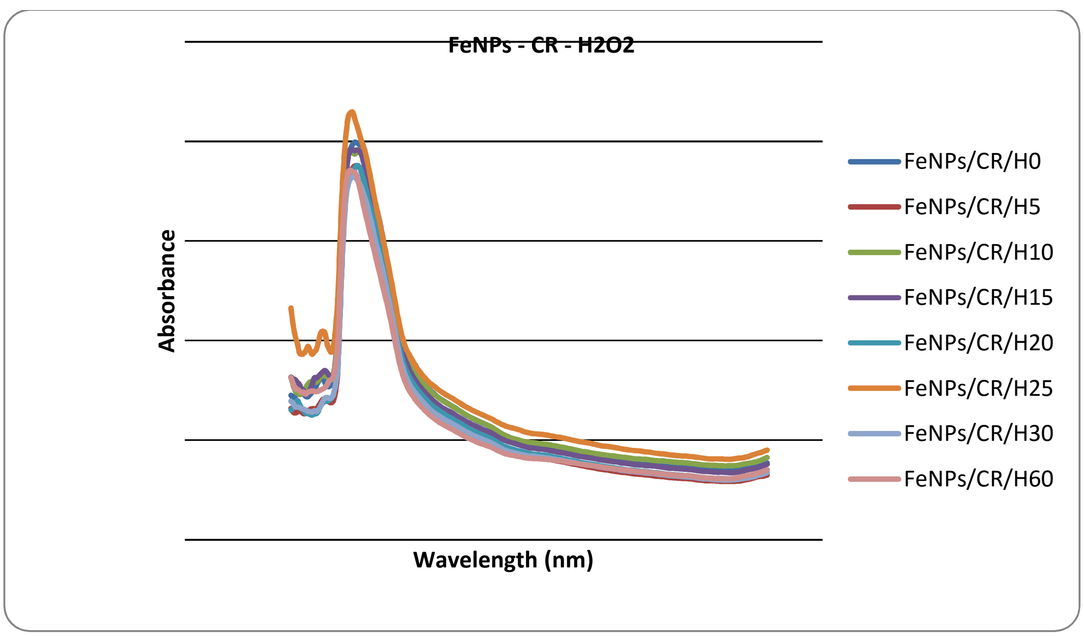

Figure 3: Absorption spectra showing degradation of CR in the presence of fenton reagent.

Figure 4 and 5 shows the photo-degradation of Congo red (CR) and malachite green (MG) with Iron (III) nanoparticles respectively in terms of absorption spectra and as a function irradiation time in the presence of hydrogen peroxide which serve as a catalyst. The photo-degradation of CR with iron (III) nanoparticles was monitored as the time increase, change in its concentration also used in the degradation efficiency, the interception of this two curves shows that the absorbance peaks of figure 4 was higher with a wavelength 332nm at 5 minutes compared to the wavelength of 320nm in figure 5 at the same time. Also their absorbance shows the same trend with the wavelength respectively. By comparing their wavelength, figure 4 degrade faster at 5 minutes with a wavelength of 332nm while figure 5 shows fast degradation at 10 minutes with 328nm. This may be due to the presence of toxic chemicals or pollutants present in MG. This also agrees with the work of Daneshva et al. (2007) that Malachite green and its reduced form, leucomalachite green are persistent in edible fish tissues for extended periods of time. Therefore,

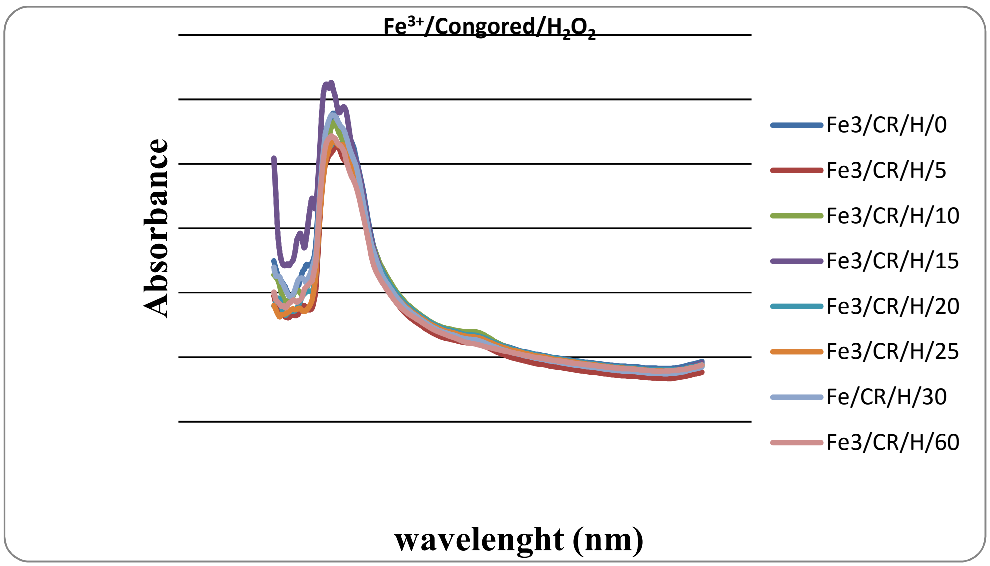

Figure 4: Absorption spectra showing degradation of CR in the presence of Fe^{3+} synthesized FeNPs and Fenton catalyst

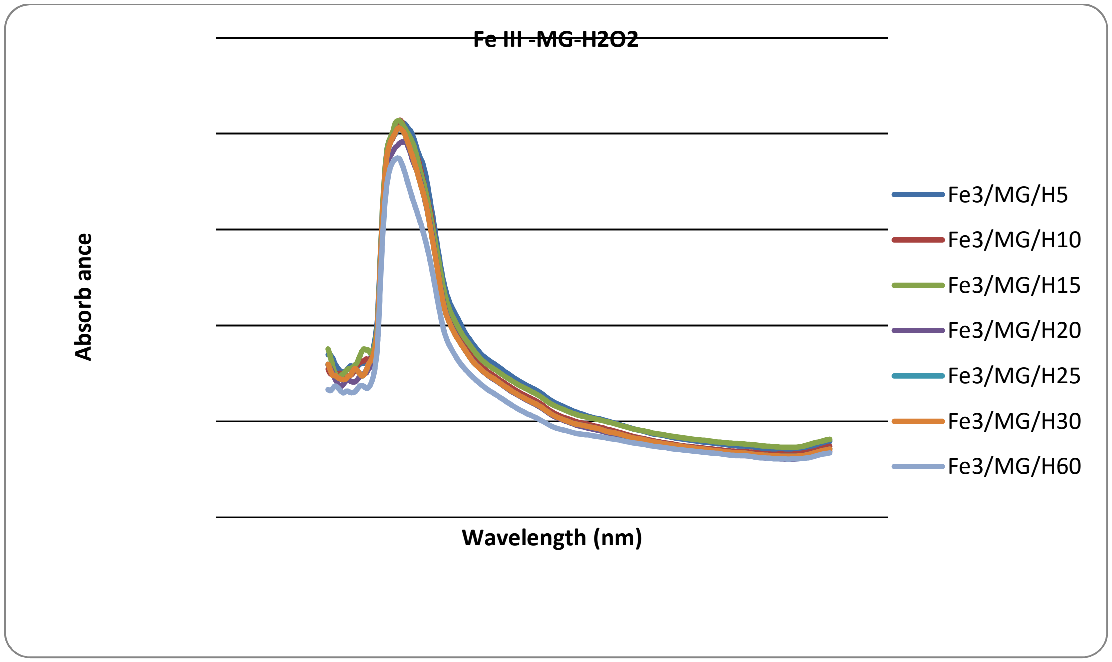

Figure 5: Absorption spectra showing degradation of MG in the presence Fe^{3+} synthesized FeNPs and fenton catalyst.

there are both environmental and human health concerns about bioaccumulation of Malachite green and leucomalachite green in terrestrial and aquatic ecosystems.

4.2.3 EFFECT OF CATALYST (H_2O_2)

It is well known that the addition of a powerful oxidizing agent such as hydrogen peroxide (H_2O_2) lead to an increase in photo-degradation efficiency (Hachem *et al.* 2001). As observed, degradation was possible in the presence of hydrogen peroxide and not in the absence of hydrogen peroxide (Figure 1). The degradation of the dyes in sunlight, visible light and low intensity UV-light was successfully used in the degradation process. It has been widely reported by Neppolian *et al.* (2002) and Zhao *et al.* (1995) that the presence of H_2O_2 enhances the photo catalytic degradation.

5.1 CONCLUSION

The study highlights the recent development in iron nanoparticles synthesized from plant extract as Fenton-like catalyst. Mango leaf extract shows an interesting potential for the synthesis of iron nanoparticles rich in iron oxide. An impressive removal capabilities of malachite green and congo red was demonstrated. The results gotten from the experiment shows that green synthesized iron nanoparticles demonstrated more effective capability as a Fenton-like catalyst in the removal of Malachite green and Congo red dye. Importantly, it was also observed that the presence of hydrogen peroxide (H_2O_2) as a catalyst enhances fast degradation and leads to a synergetic effect that increases photo-catalytic activity in the dye effluents. The synthesis and applicability of the materials in the effective degradation of Congo red and Malachite green dye was achieved.

RECOMMENDATION

Since iron nanoparticles synthesized from green plant has been found to be effective in the removal of Congo red and Malachite green dye, there is a clear need to explore plant resources other than mango leaves as well as other dyes that find wide application in textile industries

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