Colored Magnetic Nanoparticles to Improve the Sustainability of Textile Dyeing

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ABSTRACT

Current dyeing techniques face growing environmental and economic challenges due to high consumption of water, salts, auxiliaries and energy, and production of substantial amounts of industrial polluting wastewaters. This project demonstrated that colorants can be impregnated into magnetic nanoparticles to form a skin-core structure, and the resulting colored magnetic nanoparticles can be used as dyes to dye conventional textile fabrics. The colored magnetic nanoparticles can be easily dispersed in water and their movement can be controlled with a magnet. The resulting suspension was used to dye textile fabrics in the absence of salts and auxiliaries. The colored magnetic nanoparticles showed high affinity toward the fabrics, which could be due to the large surface area and high surface energy of the nanoparticles. The un-bonded dyes can be readily collected from the wastewater with a magnet, significantly simplifying the wastewater treatment process, pointing to a more environmentally friendly approach in textile dyeing.

Keywords: magnetic nanoparticles, skin-core structure, textile dyeing, environmental-friendly dye removal

1 INTRODUCTION

Current dyeing techniques in the textile industry face growing environmental and economic challenges. On one hand, the inefficiencies in dyeing processes result in the discharge of substantial amounts of dyes into wastewater, which together with the high demand on water, salts, auxiliaries generates one of the most polluting wasterwaters among various industries [1]. The released amount of un-bonded dyes depends on the type of the applied dyes, e.g., about 2% of dyes are lost when basic dyes are used, whereas up to a 50% dye loss may occur when using reactive dyes, which however take up approximately 30% of the total dye market [2, 3]. The released dyes eventually find their way into natural waterways and/or environment, posing serious environmental and health concerns due to the fact that they are persistent and recalcitrant in nature and they have been reported as a health hazard that causes skin complaints, illnesses, and cancer [1, 4]. Furthermore, the discharged dyes in the environment easily cause colouration of the water even with a little concentration, which not only makes it unsightly, but also affects aquatic ecosystems by inhibiting photosynthesis [1]. Dyes in the sediment may also be incompletely broken down by microbes and therefore produce toxic amines, leading to persistent problems [5]. For these reasons, increasingly stringent environmental legislations have been applied to the textile dyeing industry in the developed countries, forcing relocation of the textile dyeing factories to the underdeveloped conutries only because of their less stringent environmental laws as the price for economic development, but not because of possession of advanced technology for clean dyeing [2]. However, environmental problems are not solved at all.

On the other hand, a variety of biological, physical and chemical means have been adopted for the treatment of textile dyeing wastewater, such as adsorption, coagulation and/or flocculation, membrane technologies, biological treatment, oxidation, ozonation, electrochemical techniques and photocatalysis, etc [6-9]. However, these methods either create secondary pollution and disposal problems due to excessive use of chemicals and sludge accumulation, or suffer from complicated procedures and cost expensiveness [3], which, together with the high consumption of water, salts, auxiliaries and energy of the dyeing process, make the conventional dyeing techniques less cost-effective and therefore economically unviable in the U.S.

For these reasons, this work tries to develop a novel magnetic dyeing technology to address the technical and environmental issues. In this frame as illustrated in Figure 1, superparamagnetic magnetite (Fe_3O_4) nanoparticles are first synthesized as the core, which is further coated with a colorant-impregnated silica skin, yielding colored magnetic nanoparticles with a skin-core structure. The resultant colored nanoparticles would be easily dispersible in water due to the abundant hydrophilic Si-OH groups on the silica surface, and therefore they could be used as dyes to dye textile fabrics in the absence of salts and auxiliaries. It is expected that these nanoparticle dyes will have high affinity toward the fabrics because of their large surface area and high surface energy. After textile dyeing, the un-bonded nanoparticle dyes in the wastewater arising from the dye bath and washing fluid could be readily recovered with a magnet thanks to the superparamagnetic magnetite cores, which therefore significantly simplifies the wastewater treatment process. Thus, the new magnetic dyeing technology provides a much more environmentally friendly approach in textile dyeing.

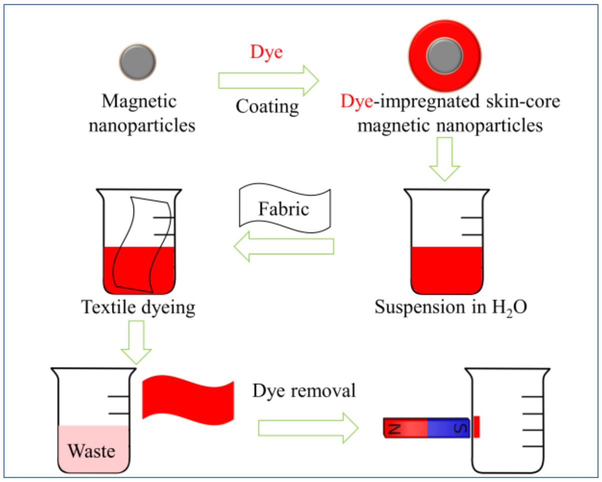

Figure 1: Schematic illustration of the magnetic dyeing technology

2 EXPERIMENTAL

2.1 Preparation of Magnetic Nanoparticles

A simple chemical coprecipitation method was utilized to prepare magnetic Fe_3O_4 nanoparticles following previously reported procedures [10]. Briefly, a mixture of 5.406 g (0.02 mol) of $FeCl_3 \cdot 6H_2O$ and 1.988 g (0.01 mol) of $FeCl_2 \cdot 4H_2O$ was dissolved in 150 mL of deionized water in a 250 mL three-necked flask, resulting in a transparent solution which was degassed with argon for 1 h. Thereafter, 20 mL of 10 M NaOH was added dropwise into the solution within 30 min under rapid mechanical stirring (500 rpm). After continuing the rapid stirring for another 1 h, the obtained black dispersion was heated up to 90 ℃ for 1 h. Upon cooling down to room temperature, the resultant magnetic Fe_3O_4 dispersion was subjected to a magnet for magnetic separation. The collected magnetic mud was then redispersed in a 200 mL of 0.5 M trisodium citrate solution and heated up at 80 ℃ for 1 h. Subsequently, the magnetic nanoparticles were collected with a magnet after precipitating in acetone to remove the excessive citrate groups that were unadsorbed on the nanoparticles, and dried at 50 ℃ in a vacuum oven. Afterwards, the obtained powder was redispersed in deionized water to yield a 2.0 wt% magnetite dispersion, which was denoted as magnetic fluid.

2.2 Synthesis of Trialkoxysilane Functionalized Dye

A classic azo dye, Disperse Red 1 (DR1), was used as the model colorant to be impregnated into magnetic nanoparticles. First, DR1 with a terminal hydroxyl group was functionalized with a trialkoxysilane group through a carbamate linkage by reacting DR1 with 3-isocyanatopropyl triethoxysilane (ICTEOS) in the presence of a tertiary amine as the catalyst following previously reported procedures [11, 12]. Briefly, 4.04 mmol (1.27 g) of DR1 and 8.08 mmol (2.0 g) of ICTEOS were dissolved in 50 mL of freshly dried tetrahydrofuran (THF) in a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser. After introducing a catalytic amount of triethylamine, the mixture was stirred and refluxed for 12 h under nitrogen atmosphere. Thereafter, the solution was cooled down to room temperature and poured into dried hexane to result in a red precipitated powder, which was collected and purified by washing with hexane/THF (9:1 v/v). Subsequently, trialkoxysilane functionalized red dye, ICTEOS-DR1, was obtained after dried at 50 ℃ under vacuum for 24 h and stored in a desiccator.

2.3 Synthesis of Colored Skin-core Magnetic Nanoparticles

Dye impregnated colored skin-core magnetic nanoparticles were synthesized following the Stöber method with some modifications [13], i.e., coating magnetic nanoparticles with the trialkoxysilane functionalized dye was performed via the hydrolysis of ICTEOS-DR1 in the presence of Fe_3O_4 magnetic nanoparticles as seeds. Typically, 5.0 mL of magnetic fuild was first diluted in 40 mL of deionized water, 160 mL of ethanol and 2 mL of aqueous ammonia solution (29 wt%) and then homogenized using an ultrasonic water bath. Afterwards, 0.5 g of ICTEOS-DR1 dissolved in 20 mL of ethanol was added dropwise into this Fe_3O_4 nanoparticle dispersion under continuous mechanical stirring at room temperature. The stirring continued for 12 h. The resultant product was collected by magnetic separation with a magnet. After washing with ethanol and water for several times and dried at 50 ℃, colored magnetic nanoparticles were obtained.

2.4 Textile Dyeing and Magnetic Removal of Dyes in the Wastewater

The colored magnetic nanoparticles were dispersed in deionized water and used as dyes for textile dyeing through a “dip-pad-dry” approach. After successive washing with acetone, ethanol and water to remove possible impurities, cotton fabrics were immersed into the colored magnetic nanoparticle suspension with a bath liquor ratio of 1:50 (w/v), and the suspension was then heated up to 90 ℃ for 1 h. After taken out of the suspension, cotton fabrics were padded on the laboratory wringer to 100% wet pickup, dried at 60 ℃ in an oven, and then thoroughly washed with excessive amount of deionized water, dried at 60 ℃, and stored in a desiccator.

After textile dyeing, the wastewater of the dye bath and washing fluid, before discarding, was subjected to a magnet to remove the un-bonded colored magnetic nanoparticle dyes from the wasterwater. These collected nanoparticle dyes were recycled for future textile dyeing.

3 RESULTS AND DISCUSSION

A simple yet effective chemical coprecipitation method was used for preparation of hydrophilic magnetic Fe_3O_4 nanoparticles. The obtained magnetic fluid was stable over a period of weeks thanks to the surface modification of the magnetite nanoparticles with citrate, which has three carboxyl groups to powerfully stabilize the nanoparticles from coagulation and/or sedimentation [10]. TEM image shows that the magnetic Fe_3O_4 nanoparticles are well dispersed, and have a size of about 13 nm (Figure 2a), suggesting that efficient surface modification of the nanoparticles was achieved. Moreover, the stable dispersion ensures successful coating with silica through the Stöber method in the next steps. The obtained magnetite nanoparticles showed superparamagnetic properties, and their movement could be controlled with a magnet (Figure 2b).

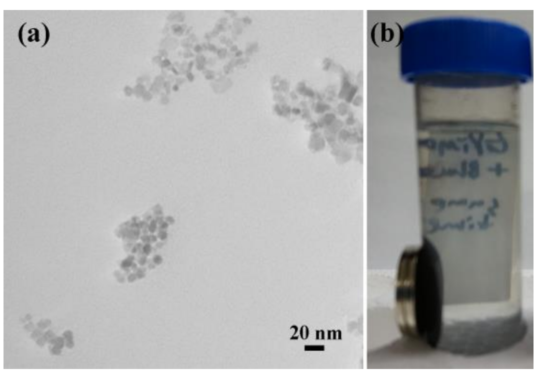

Figure 2: (a) TEM image of the magnetic Fe_3O_4 nanoparticles; (b) photograph showing the magnetic responsiveness of the magnetic fluid to a magnet.

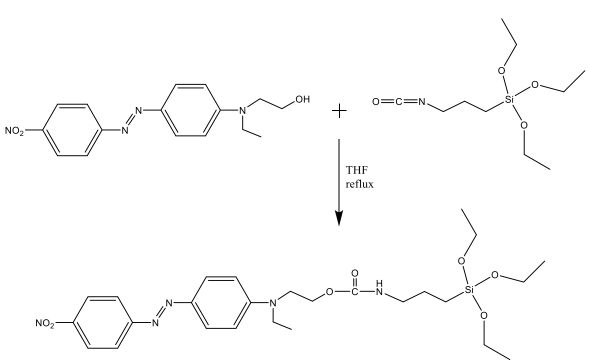

Figure 3: Synthesis route of trialkoxysilane functionalized red dye, ICTEOS-DR1 .

In order to impregnate the red dye DR1 into magnetic nanoparticles, DR1 was first successfully functionalized with a trialkoxysilane group through the synthesis route as depicted in Figure 3. The synthesized ICTEOS-DR1 was then used to coat magnetite nanoparticles through the Stöber method by base-catalyzed hydrolysis of ICTEOS-DR1 in the presence of Fe_3O_4 magnetic nanoparticles as seeds. Therefore, during the subsequent condensation of silica onto the magnetite nanoparticle cores, DR1 was successfully impregnated into the magnetic nanoparticles since it was chemically bonded with the silica skin, which could avoid any color leach in the future applications, and thus potentially enhance the color fastness.

DR1 impregnated colored skin-core magnetic nanoparticles were easily dispersible in water and the dispersion was stable over a period of weeks at room temperature (Figure 4a). The excellent stability of the nanoparticle suspension in water is believed to arise from the abundant hydrophilic Si-OH groups on the surface of the silica skin. Therefore, the colored magnetic nanoparticle suspension in water could be used as dyes to dye textile fabrics in the absence of salts and auxiliaries, which would greatly benefit the wastewater treatment.

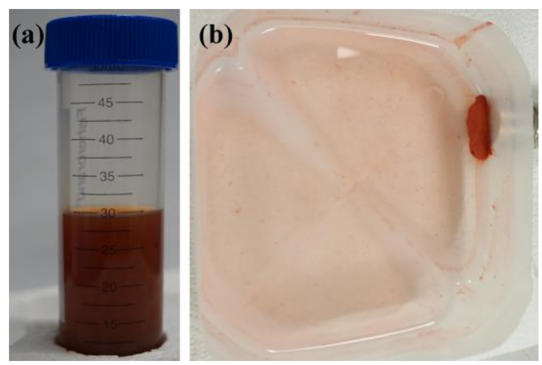

Figure 4: (a) photograph of DR1 impregnated colored skin-core magnetic nanoparticles dispersed in water; (b) photograph showing magnetic removal of colored nanoparticle dyes in the wastewater.

Cotton fabrics were successfully dyed with the colored magnetic nanoparticle suspension in water through a simple “dip-pad-dry” process. Large surface area and high surface energy of the colored nanoparticles are believed to account for the high affinity toward the fabrics.

An attractive feature of the colored magnetic nanoparticles for textile dyeing is the significantly simplifed wastewater treatment process after textile dyeing. Since there was no salts and auxiliaries in the dyeing recipe, removal of the colored nanoparticles became the only burden for wastewater treatment. Before discarding, the wastewater generated from the dye bath and washing fluid was subjected to a magnet to remove the un-bonded colored magnetic nanoparticle dyes from the wasterwater thanks to the superparamagnetic magnetite cores (Figure 4b). Moreover, these collected nanoparticle dyes could be recycled for future textile dyeing. Thus, the new magnetic dyeing technology significantly improves the sustainability of textile dyeing.

4 CONCLUSION

In this work, colorant DR1 was impregnated into magnetic nanoparticles by functionalization with trialkoxysilane first, which was then used to coat the magnetite nanoparticle cores to form a skin-core structure. The obtained colored magnetic nanoparticles were easily dispersible in water as a result of the abundant hydrophilic Si-OH groups on the surface of the silica skin, and the resulting suspension was used as dyes to dye textile fabrics in the absence of salts and auxiliaries. The colored magnetic nanoparticles showed high affinity toward the fabrics, which could be due to the large surface area and high surface energy of the nanoparticles. This new magnetic dyeing technology significantly simplifies the wastewater treatment process as the un-bonded dyes in the wastewater can be readily collected with a magnet and recycled for future use, pointing to a more environmentally friendly approach in textile dyeing.

ACKNOWLEDGEMENTS

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