Preyssler-based nanocomposite as a magnetic photocatalyst: synthesis, characterisation and its photocatalytic activity for decolourisation of rhodamine B

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In this work, the authors prepared a novel magnetic photocatalyst by grafting of Preyssler-type polyoxometalate, H_{14} [$NaP_5 W_{30} O_{110}$] onto Fe_3O_4 nanoparticles via an internal layer of silver nanoparticles. The obtained nanocomposite has been characterised by electron dispersive X-ray, transmission electron microscopy and scanning electron microscopy. The activity of the synthesised nanomagnetic photocatalyst was tested by the photocatalytic decolourisation of rhodamine B under UV light irradiation in the study's designed reactor. It was found that, compared to pure Preyssler, decolourisation of rhodamine B was occurred four times faster using the synthesised magnetic nanocomposite with easy separation. The magnetic nanocatalyst was separated after ending the reaction and recycled. It just showed 2–3% decrease in catalytic activity after four recycling.

1. Introduction: In recent years, nanomagnetic particles, have been attracted much attention due to its extinguished properties, such as special magnetic target and good biocompatibity [1]. Using nanomagnetic particles in magnetic resonance imaging, targeted therapy of cancer/HIV, bio-separation, enzyme or protein immobilisation, cell screening, nucleic acid extraction and biosensor were well documented in the past years [2–6]. One type of important magnetic nanoparticles is Fe_3O_4 that has been extensively studied because of their unique magnetic properties. Therefore a lot of researchers have focused on the preparation of magnetic nanoparticle composites [7–24] to obtain novel properties. Compared with organic analogues [7, 8], inorganic composites of magnetic nanoparticles [13–15] are considered to be easier to prepare and more safe in use. Among various used nanoparticles in inorganic composites, silver nanoparticles have attracted a great deal of interest because they can be applied for electronics [25], optics [26–29], and catalysis [30]. Various silver composite materials have been synthesised, such as silver-halide composites [31], silver/silica structures [32], and Fe_3O_4/Ag magnetic nanoparticles [33–38]. In the past decade, the catalytic properties of silver nanoparticles as well as Fe_3O_4 nanoparticles, have been gained much attention [39–42].

Nanomagnetic photocatalysts appear to be a promising material because of easy recovery by external magnetic field. An ideal magnetic photocatalyst should possess the following features: (a) high activity in photocatalytic degradation; (b) no photo dissolution during degradation; and (c) a high magnetisation for easy magnetic separation. Various kinds of surface modifications including functional groups modification and coating of inorganic metal ions have been reported for them in the last decade [43, 44].

Polyoxometalates (POMs) are a large class of metal–oxide inorganic cluster compounds consisting of transition metal atoms bridged by oxygen atoms. POMs can exist in a variety of different size and structures, and all compounds belonging to this class have been studied extensively. They possess interesting electronic and molecular properties, such as wide-ranging reduction potentials, acidities, and polarities. Based on their attractive properties, POMs have also been used in a variety of different applications, including catalysis, biomedicine, magnetism, nanotechnology, and materials science [45–48]. Among different POMs, using

heteropolyacids as a catalyst for the synthesis of fine chemicals, such as flavours, pharmaceuticals, and in food industries, has gained attention in the last decade [49]. POMs were also immobilised onto supports to prepare the supported POM photocatalysts. The supports that have been studied are including silica [50–52], mesoporous pure-silica molecular sieve [53], activated carbon [54], and zeolite [55]. Although the catalytic activity of POMs was enhanced after being supported on substrates [53–55], nevertheless, a remaining disadvantage is to have an effective separation. To this purpose, the fabrication of a magnetic nanocatalyst would allow easy recovery with an external magnet.

In this work, we prepared Preyssler-based nanocomposite as a magnetic photocatalyst (PNMP) and assessed its photocatalytic activity by decolourisation of Rhodamine B under UV irradiation. Preyssler is a remarkable POM because of: strong Bronsted acidity with 14 acidic protons, high thermal and hydrolytic stability (pH = 2–12), reusability, non-corrosiveness, high oxidation potential and greenness [56].

To the best of our knowledge, this is the first study on the using of Preyssler acid as a photolytic linker molecule of locally reduced metal ions on the surface of functionalised Fe_3O_4/Ag composite magnetic nanoparticles. The significance of the synthesised photocatalyst is its easy recovery by a magnetic field, recycling ability due to its long-term stability, cost effectiveness, and non-toxicity.

2. Experimental

2.1. Chemicals and instruments: All chemicals were purchased from Sigma Aldrich Company. Fe_3O_4 nanoparticles were prepared according to our earlier works [57]. The model VP-1450 (LEO, Co., Germany) Scanning Electron Microscope (SEM), was used for SEM analysis. It is equipped with electron dispersive X-ray analysis (EDAX) for the determination of elemental analysis. For transmission electron microscopy (TEM) analysis an LEO 912 AB instrument was used. The decolourisation of rodamine B was studied by its UV–vis spectra using Milton Roy, Spectvonic 1001 plus spectrophotometer.

2.2. Synthesis of amine-functionalised Fe_3O_4 nanoparticles: The synthesised nano-Fe_3O_4 (0.2 g) was dispersed in 20% ethanol by the ultra-sonication method and 3-triethoxysilylpropylamine was

added dropwise (0.4 ml). The mixture was stirred at room temperature for 7 h. The desired functionalised Fe_3O_4 magnetic particles were afforded as light brown suspension. An excess amount of Fe_3O_4 was washed with HCl.

2.3. Synthesis of Fe_3O_4–Ag nanocomposite: The silver nanoshell was coated onto the magnetic core by the following steps. About 1 ml of 4×10^{-2} mol/l $AgNO_3$ aqueous solution and 9.1 mg $NaBH_4$ solid were added to the well-dispersed suspension Fe_3O_4 under vigorous stirring. Then, the colloidal suspension was heated to 80°C, and $AgNO_3$ (0.15 mol/l) solution was added under vigorous stirring, followed by adding of 0.34 mol/l sodium citrate. Then, the solution was allowed to left for 1 h. The brown-black powder was separated by a magnet and dried at room temperature.

2.4. Synthesis of Fe_3O_4–Ag/PNMP: The silver-coated Fe_3O_4 nanoparticles were immersed in a solution containing 0.1 mol/l $HClO_4$ and 10^{-4} mol/l H_{14} [NaP_5 W_{30} O_{110}] (PPOM). PPOM anions were attached to the surface of Ag nanoshell via self-assembly. The obtained solids were removed by a magnet, washed and dried.

3. Results and discussion: The surface of Fe_3O_4 nanoparticles was coated by a labile layer of amine, which enabled the particle surface to remain chemically active and available for further reactions. Thus, a silver nanoshell could be deposited onto the surface of magnetic nanoparticles via the coordination of $-NH_2$ and Ag^+. The silver nanoshell was designed to act as an intermediate bond for Preyssler POM and magnetite nanoparticles so that Preyssler could be attached to the magnetic core via the self-assembly of Preyssler acid anions on silver in acidic aqueous solution.

The synthesised nanoparticles and nanocomposites were characterised by TEM, SEM and EDAX to examine the structure and morphology. TEM image of Fe_3O_4 nanoparticles has shown that the average size of Fe_3O_4 nanoparticles is about 10 nm (Fig. 1). EDAX image spectra of Ag/Fe_3O_4 nanoparticles (Fig. 2) showed that Fe and Ag elements are present in the compounds and SEM image confirms the formation of nano-Fe_3O_4–Ag (Fig. 3).

From comparing the TEM in Figs. 1 and 4, we can see that Fe_3O_4 nanoparticles coated with a layer of silver nanoparticles.

In recognition of Fe_3O_4–Ag/PNMP, EDAX image in Fig. 5 shows that it contains elements Fe, Ag, W, P and O. SEM image is also evidence for the formation of nanocomposites (Fig. 6). Finally, TEM images show the dimensions of 30–50 nm and confirm core–shell preparation (Fig. 7).

3.1. Photocatalytic decolourisation: To investigate the photocatalytic activity of the synthesised nanomagnetic composites, we have selected rhodamine B as a hazardous organic dye in
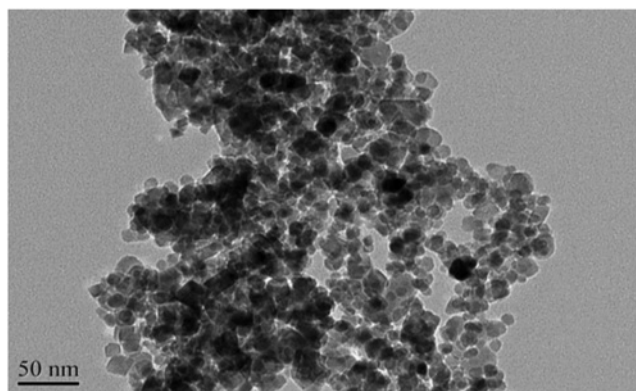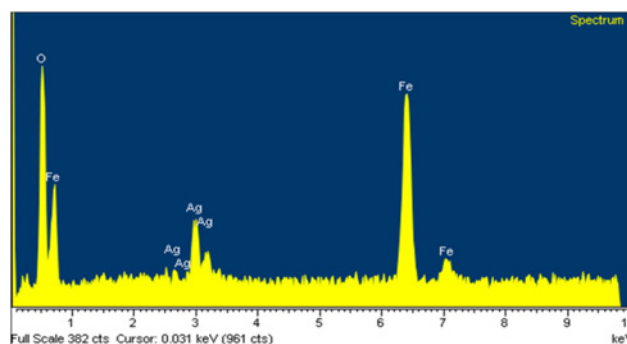
Fig. 2 *EDAX image of Fe_3O_4–Ag nanoparticles*
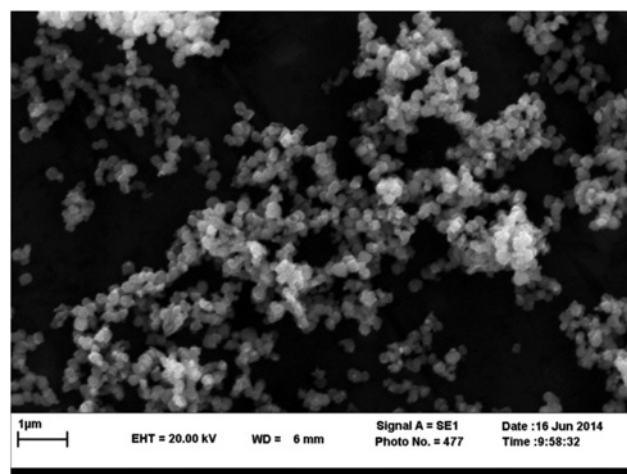
Fig. 3 *SEM image of Fe_3O_4–Ag nanoparticles*

Fig. 4 *TEM image of Fe_3O_4–Ag nanoparticles*
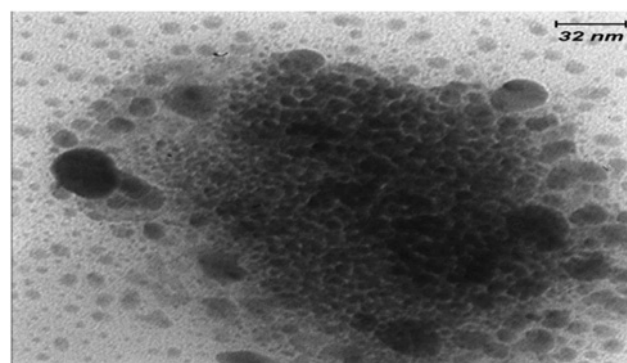
Fig. 1 *TEM image of Fe_3O_4 nanoparticles*
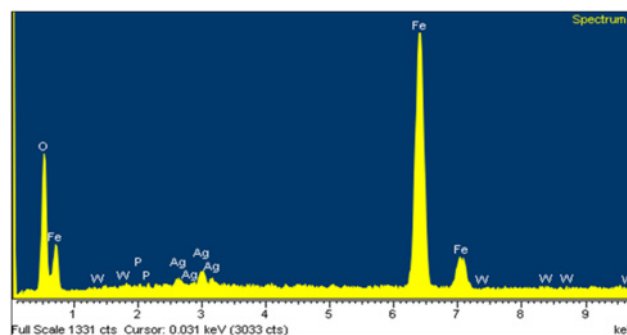
Fig. 5 *EDAX image of Fe_3O_4–Ag/Preyssler nanocomposites*
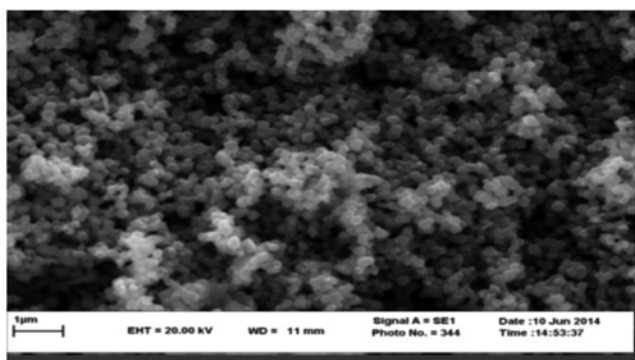
Fig. 6 *SEM image of Fe₃O₄–Ag/Preyssler nanocomposites*

Fig. 7 *TEM image of Fe₃O₄–Ag/Preyssler nanocomposite*

Fig. 8 *UV spectrum of rhodamine B decolourisation by the nanomagnetic photocatalyst*

Fig. 9 *Decolourisation efficiency of rhodamine B in the presence of different amounts of synthesised nanomagnetic composite*

Fig. 10 *Comparison of photocatalytic activity for rhodamine B decolourisation*
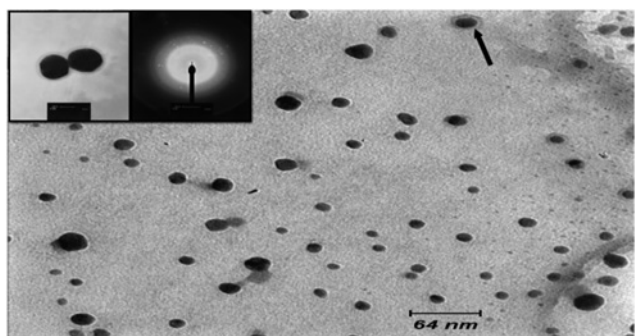
wastewaters. We have put the solution in the presence of UV light source at a distance of 15.5 cm from the light source in a designed photocatalytic reactor in our lab. Photocatalytic reactions conducted at room temperature and samples during irradiation have been under severe disruption on the magnetic stirrer. For equilibrium, a solution of Rhodamine B remained 30 min in the dark. Fig. 8 shows the amount of decolourisation increases with increasing the time to 1 h.

Using different amounts of nanomagnetic composites in rhodamine B 10 ppm, we found that decolourisation increased by increasing the amount of nanophotocatalyst up to 0.6 g and after that, it has been decreased (Fig. 9). It could be accomplished due to the increased amount of the dispersion of light, by increasing the amount of nanocatalyst. Finally, according to Figs. 8 and 9, the best time considered 1 h as well as the best amount 0.6 g. In this case, we examined and compared the ability of the synthesised nanomagnetic catalyst to eliminate of dye Rhodamine B (Fig. 10). This figure shows that in the presence of the magnetic nano-composite, decolourisation is faster and obtained 90% after 60 min. In the presence of Preyssler alone, and without any catalyst (blank solution) decolourisation was obtained 50 and 10%, respectively. The photocatalytic activity by Ag–Fe₃O₄ nanoparticles can be explained on the basis of silver being acceptor impurity in Ag–Fe₃O₄. Ag acts as an electron trap and prevents the electron–hole recombination that is an important factor in determining the photocatalytic activity [58, 59]. The photocatalytic activity of the magnetic nanocomposites in the presence of visible light, for comparison, was also checked. It was found that, without UV light, the degradation of rhodamine B is very slow and under UV light, the colour removal process of rhodamine B was significantly higher. The reuse and the stability of the nanocatalyst were studied in a very simple way. After the degradation of rhodamine B, the photocatalyst was separated easily from the solution using a magnet, while the supernatant was decanted. Then, the catalyst was washed with distilled water and reused for four times. The photodegradation of azo dye did not show any significant loss of activity (2–3%).
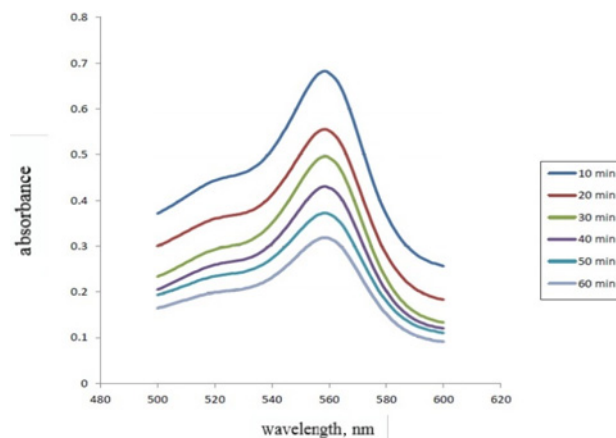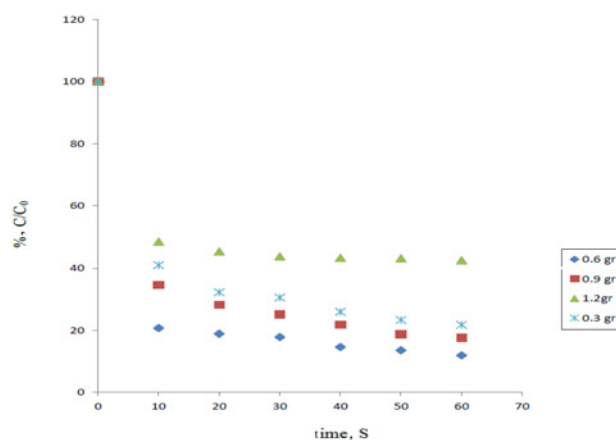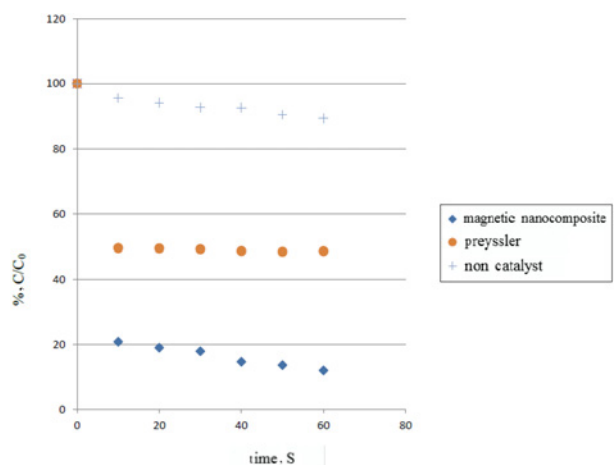
4. Conclusions: For the first time, Fe₃O₄–Ag/Preyssler nano-composites are synthesised and acted as a magnetic heterogeneous photocatalyst, in the removal of rhodamine B. Our findings showed that Preyssler anion was anchored on the surface of magnetite nano-particles via partially covered silver nanoshell. The optical solving in the newly synthesised nanocomposite has been very little and this

has been proven by the recovery of nanomagnetic photocatalyst and recycling in subsequent reactions. While the nanomagnetic photocatalyst shows good photocatalytic activity, its magnetite core enables the separation from treated wastewater by external magnetic field, which potentially provides an easier way for the photocatalyst recovery than homogenous photocatalysts.

6 References

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