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Catalytic Performance of Fe_3O_4@G2-PAMAM/MoO_3 Magnetic Nanocomposites for Degradation of 4-NP to 4-AP

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We managed to produce Fe_3O_4 magnetic nanoparticles and coat them with APTES and TEOS as a buffer. 2nd generation PAMAM dendrimers were used to cover the APTES and TEOS coated core. The surface of the multi-shelled structure was decorated with MoO_3 nanoparticles where Fe_3O_4@G2/MoO_3 dendrimer-based nanocomposites were obtained. Nanocomposites exhibit superparamagnetic characteristics. The structure of composites was assessed by SEM and EDS. TEM gives us a detailed insight about nanocomposites. Magnetic behaviours of the nanoparticles were investigated using vibrating sample magnetometry. The catalytic performance of the Fe_3O_4@G2/MoO_3 dendrimer-based nanocomposites was assessed using UV-vis spectrophotometry for the degradation of 4-Np to 4-AP. It was seen that our nanocomposites exhibit outstanding catalytical performance. K_{app} value was calculated as $5x10^{-4}$ s^{-1}.

Keywords: *Fe_3O_4, Dendrimers, MoO_3 Nanoparticles; 4-Nitrophenol*

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1. Introduction

Nitrophenol and nitrophenol derivatives were produced by different industrial and agricultural activities [1]. Nitrophenol derivatives were found to be dangerous to fresh waters and ecosystem, they are toxic to living organism in the soil and marine life [1]. Degradation of nitrophenol derivatives to aminophenol based products or filtering such products are quite costly processes. Nitrophenol derivatives tend to degrade and convert to aminophenol based derivatives. 4-Nitrophenol (4-NP) is one of the most common nitrophenol based products that can be produced by different industrial activities and were mostly used as an intermediate product [2]. However, 4-NP is quite harmful to the environment and aquatic life [1]. It is toxic to microbiota, marine life, and different animals living in the ecosystem [3]. Therefore, 4-NP should be degraded and converted to a slightly lesser harmful form which is 4-aminophenol (4-AP). Conversion of 4-NP to 4-AP in aqueous environments is an eco-friendly natural cycle [3]. Boron hydrate based products can speed up the conversion process whereas metal based catalysers also could be used. In this regard, metallic nanoparticles are an alternative solution to the problem. Nanostructures are unique materials, which find applications in different fields due to their size related properties [4]. Nanostructures are in a special size order between a single atom and bulk materials. Therefore, different properties of such structures can be tuned by changing structure, shape, and size [4]. Changing physical properties like structure, shape, and size alters different properties like electron density, electron affinity, porosity, crystal orientation, etc. Altering such properties may help researchers to adjust different intrinsic properties

of materials such as optic, electrical, magnetic characteristics, etc. [4] Among those, metallic nanoparticles were found to be interesting due to their fascinating characteristics. They were found to be stable and durable most of them are reusable in different applications. They also illustrate good electronic, magnetic and catalytic performance [5]. Different reports show that metallic nanoparticles and nanostructures may have significant catalytic properties where different nanoparticles were reported for different catalytic activities [6]. For example, gold nanoparticles were one of the most popular nanoparticles used in catalytic activities [7]. Nanoparticles like AgO, CuO, ZnO NiO, Fe_3O_4 could also be used in catalytic degradation applications[8–12]. However, some nanoparticles may also have toxic effects on the environment and/or living organisms. Some nanoparticles can accumulate in living organisms which may trigger long term side effects, especially on humans such as Alzheimer, anaemia, suppression of the immune system, etc. [11,13–16] Therefore, removing the nanoparticle after catalytic degradation is also important to minimize the possible side effects [17]. Different methods were proposed to collect nanoparticles and catalytic materials from an aqueous environment after the catalysis process. Filtration methods were common methods which were proposed by different research groups. The filtration method is quite expensive and is not reusable. Filtration methods are not selective methods that can filter both nanoparticles and other elements in the water. Such a case increases the filtration cost and disables us to reuse the nanomaterials which were previously used for the catalytic reactions. In this regard, magnetic nanoparticles can be an option as catalytic materials [17]. Magnetic nanostructures could have multifunctional properties where nanostructures with both magnetic and catalytic properties could be synthesized. Therefore, catalysis material could be collected from the aqueous media via a magnet [17]. Such a method reduces the filtration cost, and it enables users to reuse the catalytic material at various times [17].

With these motivations, we synthesized Fe_3O_4@G2/MoO_3 magnetic nanocomposites and used them for the reduction of 4-NP to 4-AP. We produced Fe_3O_4 magnetic core with hydrothermal synthesis and coated it with APTES and TEOS. The magnetic core was then covered with G2-PAMAM dendrimers. PAMAM dendrimers were then decorated with MoO_3 nanoparticles where Fe_3O_4@G2/MoO_3 magnetic nanocomposites were produced. Structural characterization of the nanocomposites was performed using different microscopic and spectroscopic methods. Catalytic performance was checked using a UV-vis spectrophotometer. It was seen that our nanocomposite structure shows good catalytic activity. It also exhibits outstanding superparamagnetic characteristics where nanoparticles could be collected via a magnet. Such a case illustrates that nanoparticles could be magnetically filtrated, and they are reusable for different applications.

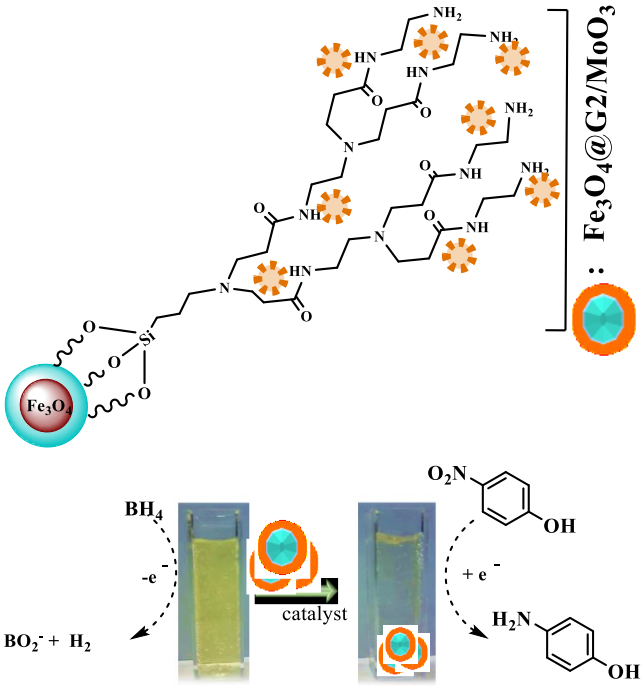

Figure 1: Schematic illustrating the Fe_3O_4@G2/MoO_3 magnetic nanocomposites and catalysis process.

2. Experimental

2.1. Materials and reagents

$FeCl_3.6H_2O$, $FeCl_2.4H_2O$, tetraethylortasilicate (TEOS), (3-Aminopropyl) triethoxysilane (APTES), 28% ammonia (NH_3), methylacrylate, ethylenediamine, ethanol, methanol were purchased from Sigma-Aldrich. Molybdenum (VI) oxide (nanopowder, 100nm) were obtained from Aldrich.

2.2. Production Synthesis of Fe_3O_4@G2/MoO_3 magnetic dendrimer

Fe_3O_4 magnetic dendrimers were produced using the same method which was reported in our previous reports [18,19]. To synthesize MoO_3 doped magnetic dendrimers 0.2 g Fe_3O_4@G2dendrimers were dissolved in 20 mL methanol and sonicated for 20 mins. 20 mg of MoO_3 nanoparticles were added to the Fe_3O_4@G_2 suspension and the mixture was stirred for 24 h under N_2 blow where dendrimer attachment occurred. The final product which was Fe_3O_4@G2/MoO_3 was collected by a magnet and washed using ethanol and pure water. The resulting product was kept in a vacuum oven at 40 ^{o}C for 12h.

3. Results

3.1. Characterization of Fe_3O_4@G2/MoO_3 PAMAM dendrimer

FTIR, XRD, TGA and elemental analysis results about Fe_3O_4 magnetic cores and PAMAM dendrimers were presented in our previous study [18,19]. Figure 2 illustrates SEM images of Fe_3O_4@G2/MoO_3 nanocomposites. It was seen that Fe_3O_4 nanoparticles exhibit high magnetic characteristics. Therefore, they have agglomeration tendencies where most of the particles were agglomerated. Moreover, dendrimerization process was found to be successful where spherical nanoparticles in uniform structure could be seen.

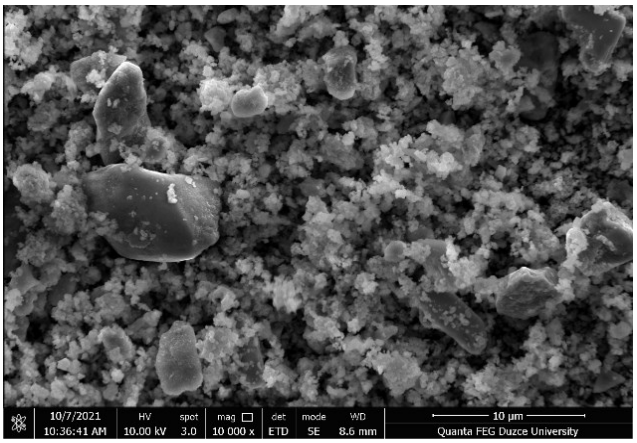

Figure 2: SEM image of SEM image of Fe_3O_4@G2/MoO_3 nanocomposites.

EDX spectrum of Fe_3O_4@G2/MoO_3 nanocomposites was presented in Figure 3. Apparent Fe, O, Mo, C Si and N related peaks could be identified. Fe and O related peaks were originated from Fe_3O_4 nanoparticle core. Mo related peaks originated from MoO_3 nanoparticles. Si, C and N related peaks originated from APTES and TEOS support layers. No contamination related peaks were observed in the EDX spectra; therefore, we concluded that our nanoparticles are quite pure.

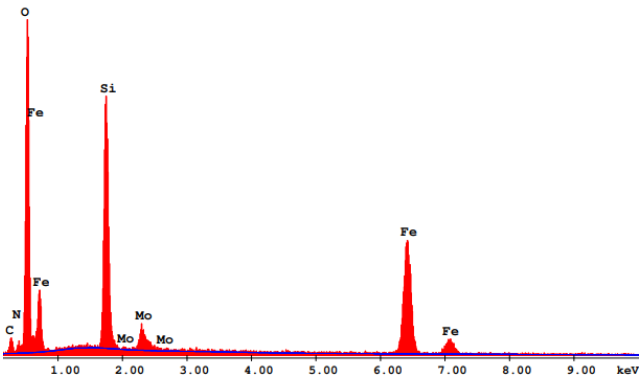

Figure 3: EDX spectrum of Fe_3O_4@G2/MoO_3 nanocomposites.

TEM images of Fe_3O_4@G2/MoO_3 nanocomposites were presented in Figure 4. The figure illustrates that nanocomposites were in a branchy structure where Fe_3O_4 nanoparticles and Fe_3O_4@G2/MoO_3 nanoparticles could be identified with a visual inspection. Probably PAMAM dendrimers and magnetic Fe_3O_4 nanoparticles in composite structure cause a branch like agglomeration. The dark spots in the image are probably MoO_3 nanostructures attached to the dendrimers. Lighter spots in the Fe_3O_4@G2/MoO_3 nanocomposites were thought to be the Fe_3O_4 magnetic cores. The weighting of the Mo atom in TEM was expected to be slightly higher than the Fe atoms. Hence, seeing such an atom related colour difference is quite normal.

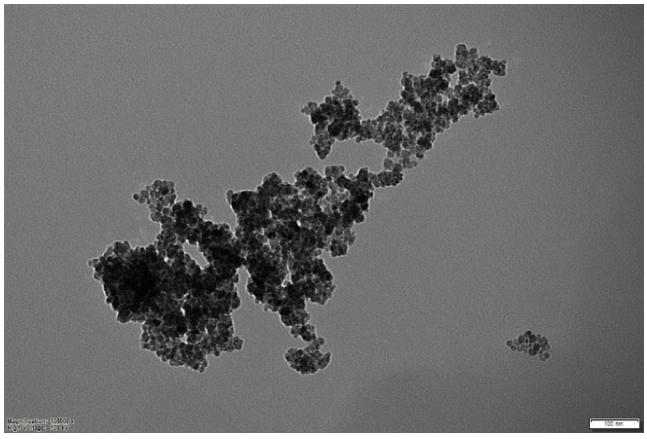

Figure 4:TEM image of Fe_3O_4@G2/MoO_3 nanocomposites.

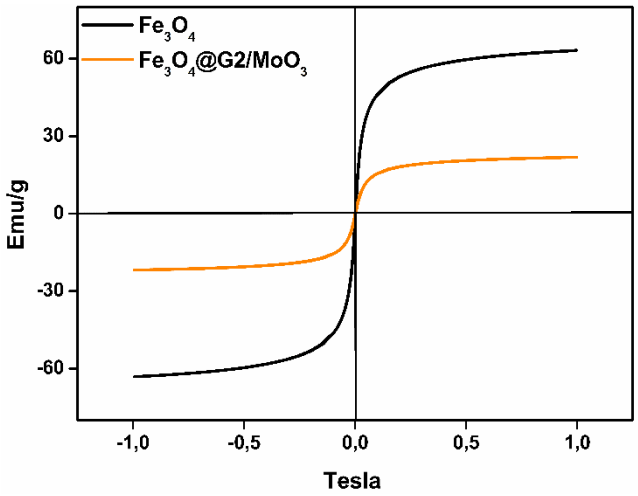

Figure 5: Magnetic hysteresis results of Fe_3O_4 magnetic nanoparticles and Fe_3O_4@G2/MoO_3 nanocomposites.

Magnetic properties of the Fe_3O_4@G2/MoO_3 nanocomposites were investigated using VSM where the Fe_3O_4 magnetic nanoparticle core and Fe_3O_4@G2/MoO_3 nanoparticle composite structures were assessed using vibrating sample magnetometry. VSM results illustrate that Fe_3O_4 nanoparticles and Fe_3O_4@G2/MoO_3 nanocomposites exhibit superparamagnetic characteristics. It was seen that covering the magnetic core with multiple covers does not change the overall magnetic characteristics. Magnetic

saturation values for Fe_3O_4@G2/MoO_3 and Fe_3O_4@G2/MoO_3 nanocomposites were found to be 63.7 emu/g and 21.87 emu/g, respectively. A slight decrease in the magnetic saturation value was observed; however, magnetic coercivity characteristics were not changed after multiple covers and Mo nanoparticle decoration processes.

3.2. Catalytic activity

The work illustrating the catalytic performance of Fe_3O_4 magnetic nanoparticles for the degradation of 4-NP to 4-AP was presented in our report [19]. In this work, we investigated the catalytic performance of the Fe_3O_4@G2/MoO_3 magnetic nanocomposites for the reduction of 4-NP to 4-AP in the presence of $NaBH_4$. The investigation was performed in the presence of 10 mg catalyser (Fe_3O_4@G2/MoO_3) in an aqueous media with 0.1 mM 4-NP and 0.2 M $NaBH_4$. UV scan was performed between 250 nm and 400 nm. At the beginning of the process, an apparent peak at 400 nm wavelength appeared. The peak was associated with 4-NP. After the presence of $NaBH_4$, another peak appeared at around 310 nm wavelength. The peak was attributed to 4-AP formation. Before the addition of the catalyser 4-NP was tracked using a UV spectrophotometer. However, no alteration in the peak position and intensity was observed. On the other hand, the presence of catalytic material triggered the 4-AP related peak formation. The peak observed at 325 nm wavelength was attributed to the 4-AP conversion of 4-NP without side reactions.

Figure 6 illustrates the UV spectrophotometer spectrum results obtained for the catalytic activity of Fe_3O_4@G2/MoO_3 magnetic nanocomposites for the degradation of 4-NP to 4-AP. After presence of Fe_3O_4@G2/MoO_3 magnetic nanocomposites, 93% of the 4-NP was degraded to 4-AP in an hour. The concentration of $NaBH_4$ is extremely high compared to 4-AP; hence, $NaBH_4$ concentration was assumed to be stable. Thus, alteration of the 4NP concentration was accepted as a pseudo first order reaction. Reaction rate "k" was calculated regarding the time dependent linear rate of (A_t/A_0) where equations 1, 2 and 3 was used.

Here ϑ reaction speed, n is the reaction order, C_t is time dependent concentration, C_0 initial concentration, k reaction rate coefficient, t time, A_t time dependent absorbance value, A_0 is the absorbance when t= 0.

$$\vartheta = dC/dt = -k * C^n \quad (1)$$

n = 1 assuming;

$$\int_{C0}^{Ct} dC/C = -k \int_0^t dt \quad (2)$$

$$\ln(\frac{Ct}{C0}) = \ln\left(\frac{At}{A0}\right) = -k * t \quad (3)$$

Table 1 and Figure 6 illustrate the results obtained from our assessments. The reaction rate coefficient for Fe_3O_4@G2/MoO_3 magnetic nanocomposites was found as K_{app}=5x10^{-4} s^{-1}. Our result was found to be quite good compared to the previous results reported by different studies (please see Table 1).

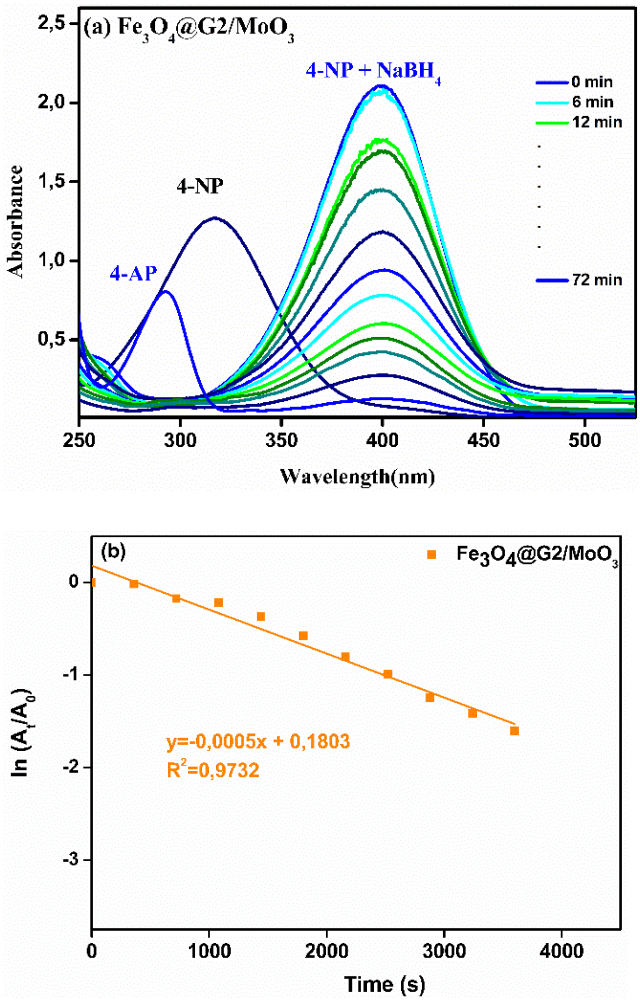

Figure 6: UV–vis spectra obtained in the 4-NP reduction in the presence of Fe_3O_4@G2/MoO_3 (a), nanostructures and plot of the In (A_t/A_0) against the reaction time (b).

Table 1. Comparison of the results of this work with other reported methods in the reduction of 4-NP to 4-AP.

Catalyst	**The amount of catalyst**	**4-NP**	**$NaBH_4$**	**k_{app}**	**Ref.**
Fe_3O_4@APTES@PAMAM-Ag	3 mg.mL^{-1}	0.005 M	0.2 M	0.672 min^{-1}	[20]
FPP/Au	1 mg.mL^{-1}	0.0006 M	0.1 M	3.75x10^{-3}s^{-1},	[21]
Fe3O4@SiO_2/APTES-Au	10 mg	0.1 mM	0.2 M	1.43x10-2 s^{-1}	[22]
Fe_3O_4@Cu	1 mL	1.499 mM	1.316 mM	0.04574 s^{-1}	[23]
Fe_3O_4@MIL-100(Fe)/Ag	5 mg.mL^{-1}	100 µM	0.3 M	2.83x min^{-1}	[24]
Fe_3O_4@G2/Au/Ag	10 mg	0.1 mM	0.2 M	6x10^{-3} s^{-1}	[19]
Fe_3O_4@G2/MoO_3	10 mg	0.1 mM	0.2 M	5x10^{-4} s^{-1}	TW

TW: This Work

4. Conclusion

In the study, we produced Fe_3O_4 nanoparticles and used them as a magnetic core to produce Fe_3O_4@G2/MoO_3 magnetic nanocomposites. Fe_3O_4 magnetic nanoparticles were covered with APTES and TEOS to produce a buffer for the G2 PAMAM dendrimers. A G2-PAMAM dendrimer covered structure was decorated with MoO_3 nanoparticles where Fe_3O_4@G2/MoO_3 magnetic nanocomposites were produced. Structural characterization methods applied to nanocomposites confirmed that nanocomposites were produced in the desired form. Spectroscopic investigations illustrate Fe, O, Mo, Si and C related peaks which were coherent with our scenario. Fe_3O_4@G2/MoO_3 magnetic nanocomposites were used for the degradation of 4-NP to 4-AP in the presence of $NaBH_4$. It was illustrated by UV-vis investigations that our nanocomposites are eligible to catalyse the degradation reaction. The reaction rate coefficient was found to be quite high compared to the results previously published in the literature. It was concluded that magnetic nanocomposites have the potential to be used in the degradation of 4-NP to 4-AP as a catalyser.

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