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Iron oxide nanoparticles synthesis through a benign approach and its catalytic application ☆

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Summary   Synthesis of iron oxide nanoparticles was carried out through an environmental benign route using tannic acid as reducing and capping agent. The TEM image shows the details of the poly-dispersity in size of the iron oxide nanoparticle and average diameter of the particles range in between 30 and 50 nm. XRD result rule out that iron oxide nanoparticle is a mixed phase constituted by Fe^{+2} and Fe^{+3} ions. The average size of the particle determined from XRD data is 45.6 nm which is agreeable with the finding obtained from TEM images. This particle of iron oxide is used for the degradation of p-cresol and it successfully degraded p-cresol. Catalytic property of the iron oxide nanoparticle was also investigation using methylene blue as role model dye. Degradation of methylene blue dye was studied in presence of $NaBH_4$ and the degradation reaction followed first order kinetics with rate constant value of $1.6 \times 10^{-3}\,min^{-1}$. The rate constant of the reaction in absence of iron oxide nanoparticles is $4 \times 10^{-4}\,min^{-1}$, this result confirmed the catalytic nature of as such prepared iron oxide nanoparticles.

Introduction

In last few decades, nanoparticles (NPs) have attracted much attention in various field of science and technology due to its unique properties like optical, surface effects, quantum confinement effect etc. Because of these

properties, NPs have wide application in field of catalysis (Guo et al., 2004; Rosei, 2004). Scientist have reported many ground breaking works in the field of NPs. Various methods were developed for the fabrication of NPs, but looking from the present scenario of our environment, methods in which used of safer, less toxic and easily degradable chemicals are highly recommended (Vigneshwaran et al., 2006).

Tannic acid which is a polyphenol derivative of plants was used as reducing and stabilizing agent for the synthesis of iron oxide NPs in alkaline medium (Yi et al., 2011). Tannic acid is a mixture of gallotannin and gallic acid esters of glucose (Wei and Qian, 2008). Because of its antioxidant

property it is used as capping agent. The utilization of toxic solvent and harsh chemicals is completely ignored during the synthesis process.

Materials and experiments

Materials

Ferric nitrate nonahydrate, Tannic acid (T.A) ($C_{76}H_{52}O_{46}$, $M_w = 1701$) and NaOH were all purchased from Sigma—Aldrich. p-cresol and methylene blue were obtained from Merck. All the solutions required in the synthesis of silver nanoparticles were prepared using double distilled water. Freshly prepared tannic acid solution and NaOH solution were used for the fabrication of iron oxide nanoparticles.

Experiments

Synthesis of nanoparticles
0.1% of iron oxide nanoparticle is synthesized using tannic acid in presence of sodium hydroxide. In this process, 0.05 g of iron is dissolved in 50 ml of double distilled water to it 8 ml of 0.004 M tannic acid was added followed by 2 ml of NaOH (0.5 M) .The whole of reaction mixture was stirred for 2 h. Change in colour of the solution (light yellow to black) indicates the formation of nanoparticles

Study of degradation of p-cresol and methylene blue
To 20 μl of 50 ppm p-cresol, 25 μl of iron oxide NPs was added and the volume of the reaction mixture was made up to 2 ml by adding double distilled water in a 3 ml capacity quartz cuvette. This reaction mixture was monitored under UV—vis spectroscopy at 40 °C.

Degradation of methylene blue was also study using UV—vis spectroscopy. To 25 μl of 10^{-3} M methylene blue, 30 μl of iron oxide NPs was introduced followed by 10 μl of 0.1 M NaBH$_4$ solution in the 3 ml cuvette. Later the volume of the reaction mixture was made up to 3 ml by adding double distilled water. This degradation process was studied at room temperature.

Characterization

Characterization was done using Perkin Elmer UV-Vis spectrophotometer, TECNAIG^2-30 U TWIN transmission electron microscope operating at 300 KV, Phillip X⸳PERT XRD
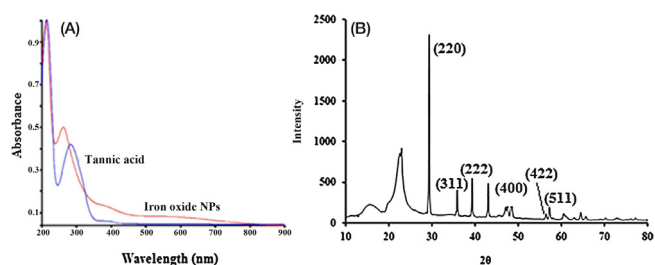

Figure 1   (A) UV-Vis spectra and (B) XRD of iron NPs.

instrument and SEI quanta 250 model scanning electron microscope.

Result and discussion

Particle of iron oxide nanoparticle synthesized using tannic acid and sodium hydroxide seems to be very stable in aqueous medium as it remains unsettled for more than eight months. UV—vis spectra of tannic acid and iron oxide NPs is given in Fig. 1(A). XRD confirmed the crystalline nature of the NPs and result out that iron sample is mixed phase of iron oxide constituted by Fe^{+2} and Fe^{+3} ions, indicating that the particles is a mixture of magnetite(Fe_3O_4) and hematite (Fe_2O_3) (Mamani et al., 2013; Mohammadi and Barikani, 2014; Gamarra et al., 2014) as show in Fig. 1(B).

Average size of the NPs is calculated using Scherrer's Eq. (1) and it is found to be 45.6 nm (Wu and Chen, 2010).

$$t = \frac{0.9\lambda}{B\cos\theta_B} \tag{1}$$

From the HRTEM image it can be concluded that particle size is in the range of 30—50 nm and SAED pattern highlights the crytallinity of NPs given in Fig. 2(A and B). Fig. 2(C) shows the SEM image of iron oxide NPs. SEM images shows a spiky structure/directional growth of NPs which may be due to the agglomeration of NPs (Onoda and Hench, 1979; Aksay et al., 1983).

Particles as fabricated are used for the degradation of p-cresol and methylene blue. Fig. 3(A) shows the UV—vis spectra of p-cresol degradation using iron oxide NPs, p-cresol show absorbance peak at 279 nm and decrease in absorbance of this peak indicates the degradation of P-cresol. Complete degradation of p-cresol takes place in 38 h. Even though this process consume time but it is a safer and benign way for treating p-cresol. To understand the nature of interaction between p-cresol and iron oxide NPs, degradation of p-cresol was studied using IR spectroscopy. IR of
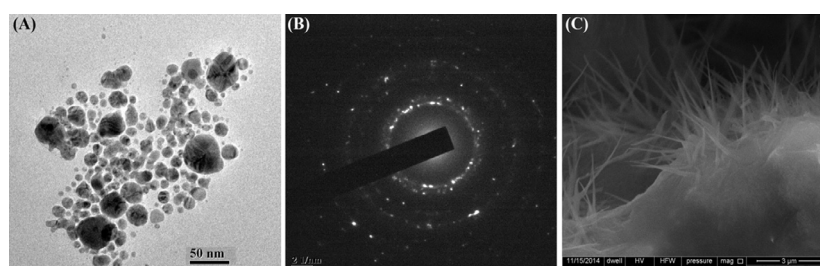

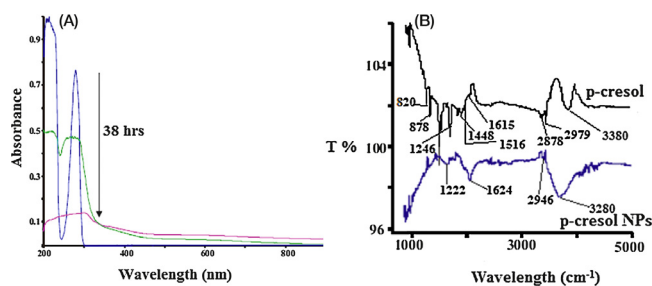**Figure 2**   (A) TEM (B) SAED pattern and (C) SEM images of iron NPs.

Figure 3 (A) UV—vis spectra of p-cresol degradation and (B) IR spectra of p-cresol and p-cresol treated with NPs.
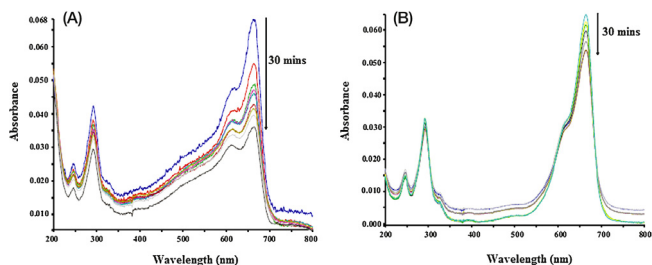

Figure 4 UV—vis spectra of degradation of methylene blue in (A) presence of iron oxide and (B) absence of iron oxide.

p-cresol composed of bands at $3380\,cm^{-1}$ which is of O—H stretching, symmetric and asymmetric stretching of CH_3 at $2979\,cm^{-1}$ and $2878\,cm^{-1}$ respectively, bands in range of $1516-1448\,cm^{-1}$ can be attributed to C=C aromatic stretching, C—O stretching at $1222\,cm^{-1}$ and $1246\,cm^{-1}$, bands at $878\,cm^{-1}$and $820\,cm^{-1}$ is of para substitution of aromatic ring (Pavia et al., 2015). Most of these bands are shifted when treated with NPs indicating strong interaction between NPs and p-cresol. After treating with NPs, O-H stretching has been shifted to $3280\,cm^{-1}$ which may be due to the formation of acid .From the findings obtained from IR and as reported earlier in literature, it can be concluded that p-cresol is degraded and by product may be benzoic acid (Londry et al., 1997; Hopper and Taylor, 1975).

Methylene blue (M.B) degradation was also studied using iron oxide NPs. M.B show absorption peak at 664 nm. Fig. 4(A) shows the degradation of methylene blue in 30 min by iron oxide NPs in presence of $NaBH_4$, this degradation reaction followed first order kinetic with rate constant of $1.6 \times 10^{-3}\,min^{-1}$.

To understand the role of iron oxide in the degradation process the reaction was study in absence of NPs but in presence of $NaBH_4$, degradation rate is very slow (rate constant decreases to $4 \times 10^{-4}\,min^{-1}$) as given Fig. 4(B). From this it can be conclude that iron oxide NPs plays the role of catalyst, the reaction take place though electron relay redox process. $NaBH_4$ reacts with NPs to give H on the metal surface and transfer a surface—hydrogen species to surface of NPs resulting in the increase of rate of reduction (Tanyu et al., 2014). This catalytic property of iron oxide NPs is due to the high surface to volume ratio which significantly increases the surface activity (Roduner, 2006).

Conclusion

Iron oxide NPs were successfully synthesized using tannic acid in presence of NaOH. Particles of iron as such prepared are very stable and have good catalytic property. Iron oxide NPs successfully degraded p-cresol in 38 h and acts as catalyst in degradation of methylene blue in presence of $NaBH_4$.

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