Facile synthesis of γ-Fe_2O_3 nanoparticles integrated $H_2Ti_3O_7$ nanotubes hybrid structures as magnetically separable dye-removal catalyst

Narayani Harsha, K. V. Swathi Krishna, Neeroli K. Renuka, Satyajit Shukla

†Electronic Supplementary Information (ESI)

(A)

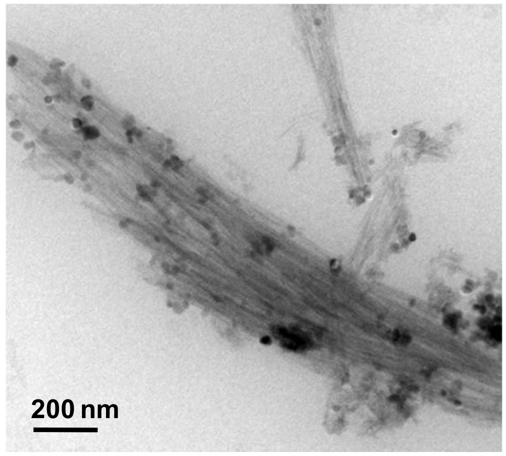

Fig. S1 Low magnification TEM image of HTNF-5 sample.

The low magnification TEM image of HTNF-5 sample is provided in Fig. S1. It is clearly evident that the γ-Fe_2O_3 nanoparticles are attached to the ends of nanotubes which appear to be a typical phenomenon.

(B) In typical experiments, 0.05 g of γ-Fe_2O_3 nanoparticles and 0.95 g HTN were added separately to 125 ml distilled aqueous solution at the neutral solution-pH (~6.5). The final solution-pH after stirring the each suspension for 1 h was measured. Similar measurements were also carried out with the combined additions of both the samples. (Note: The addition of HTN is followed by that of γ-Fe_2O_3 nanoparticles.). The obtained initial and final solution-pH values are tabulated in the Table S1.

Table S1 Variation in the solution-pH as obtained for the different samples.

Sample	**Initial solution-pH**	**Final solution-pH**
Pure HTN	6.5	4.5
γ-Fe_2O_3 nanoparticles	6.5	6.2
Pure HTN + γ-Fe_2O_3 nanoparticles	6.5	4.0

It is noted that the final solution-pH is decreased to ~4.5 for the pure HTN sample which is due to both the chemisorption of OH^- ions and its Bronsted acidic nature. With the additional presence of γ-Fe_2O_3 nanoparticles, the following chemical reactions may occur simultaneously.

(a) Chemisorption of H^+ ions from the surrounding solution since the point-of-zero charge of γ-Fe_2O_3 nanoparticles is ~5.0.
(b) Neutralization of any negative charge on the surface of γ-Fe_2O_3 nanoparticles.
(c) Further dissociation of pure HTN to H^+ and $Ti_3O_7^{2-}$.

The chemical reactions (a) and (b) would tend to increase the solution-pH; while, the chemical reaction (c) would tend to decrease it. As a consequence, the final solution-pH of ~4.0 as obtained with the combined addition of γ-Fe_2O_3 nanoparticles and pure HTN is the net result of the effects of chemical reactions (a) to (c). The lower value of final solution-pH with the combined addition of γ-Fe_2O_3 nanoparticles and pure HTN compared with that obtained using the pure HTN suggests the dominance of the effect of chemical reaction (c) over that of chemical reactions (a) and (b). This strongly supports further dissociation of pure HTN to H^+ and $Ti_3O_7^{2-}$ in the presence of γ-Fe_2O_3 nanoparticles.

(C)

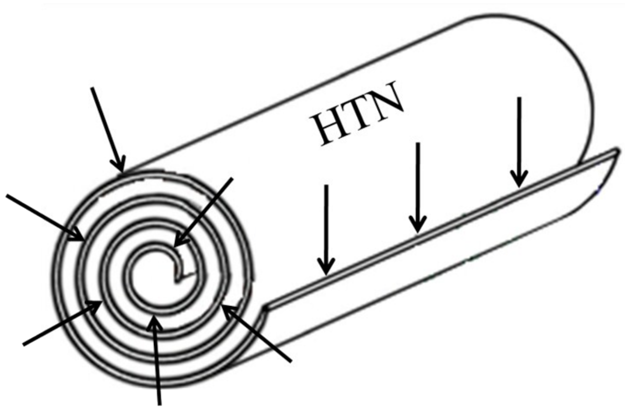

Fig. S2 Schematic diagram describing the potential sites for the operation of ion-exchange mechanism as indicated by the arrows.

(D)

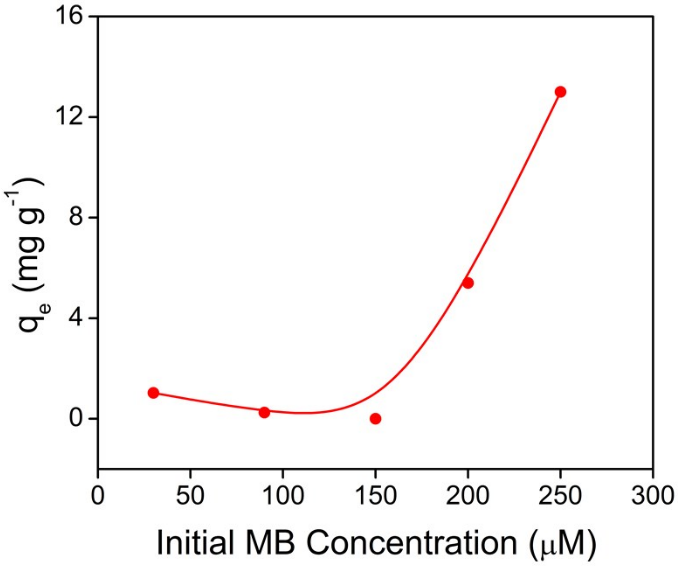

Fig. S3 Variation in q_e as a function of initial MB concentration as obtained at the initial solution-pH of ~10 for the γ-Fe_2O_3 nanoparticles.