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Layer-by-layer assembly of iron oxide magnetic nanoparticles decorated silica colloid for water remediation

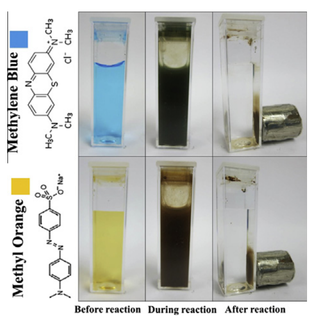
By Hui Xin Che [a], Swee Pin Yeap [a], Abdul Latif Ahmad [a], JitKang Lim [a,b,*]

[a] School of Chemical Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang 14300, Malaysia
[b] Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA

HIGHLIGHTS

- Layer-by-layer assembly of magnetic nanoparticles, polyelectrolyte and silica colloid nanocomposite.
- Nanocomposite with good colloidal stability, exhibits magnetic and catalytic bifunctionalities.
- Catalytic degradation dominates over electrostatic interactions for dye removal.
- Nanocomposite remained catalytically active after 6 months of storage.

GRAPHICAL ABSTRACT



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ABSTRACT

Silica colloid–polyelectrolyte–iron oxide nanocomposite with both magnetic and catalytic properties has been synthesized via layer-by-layer assembly. Dynamic light scattering (DLS) and electrophoretic mobility measurements were employed to monitor the evolution of these structures from silica colloid to silica colloid–polyelectrolyte–iron oxide composite. In addition to DLS, transmission electron microscope was used to investigate the morphology of nanostructure synthesized at each stage. The final structure formed show good colloidal and catalytic stability and real time magnetophoretic response under low magnetic field gradient. Here we demonstrated the potential environmental engineering application of this nanocomposite by taking organic dye, Methylene Blue (MB) and Methyl Orange (MO), as our model system. The experiment was conducted by testing the capability of nanomaterials synthesized at each stage, namely silica colloid, polyelectrolyte-functionalized silica colloid (silica–PDDA), and silica colloid–polyelectrolyte–iron oxide composite (silica–PDDA–IOMNPs), for dye removal. By taking into account the electrostatic interactions between the dye molecules and the as-synthesized nanomaterials, we verified that silica colloid–polyelectrolyte–iron oxide composite is superior for pollutant removal from aqueous environment mainly due to its catalytic property. We rationalized our finding by performing (1) Langmuir and Freundlich adsorption analysis, and, (2) pseudo-first-order and pseudo-second-order kinetic study for all three species of aforementioned nanomaterials. The reusability of silica–PDDA–IOMNPs nanocomposite was tested by subjecting this nanomaterial for multiple cycle of dye removal process. This hybrid material remained catalytically active after six months of storage.

* Corresponding author. Address: School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia. Tel.: +60 4 599 6423; fax: +60 4 599 1013.

E-mail address: chjitkangl@eng.usm.my (J. Lim).

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1. Introduction

Magnetic nanoparticle has been used extensively for biological [1–4] and environmental [5,6] applications mainly due to its unique catalytic and magnetic properties with extremely high surface-to-volume ratio [6]. Iron oxide magnetic nanoparticles (IOMNPs) are sometimes used solely, without further modification, to remove heavy metals from industrial wastewater [7]. However, pure inorganic magnetic iron based nanoparticle can easily form large aggregate driven by inter-particles van der Waals and magnetic attractions, and hence negate the benefits associated to its nanoscopic dimension [8]. In addition, the nanotoxicity exhibited by IOMNPs [9] has also discouraged the large scale implementation of this nanomaterial for environment remediation. Therefore, surface modification of IOMNPs is necessary to promote colloidal stability of the particles suspension formed and also minimize nanotoxicity effect in order to enhance its functionality for targeted application [10]. The most popular way to achieve this target are either surface modified IOMNPs with organic [11,12] or inorganic material [13,14] or integrating the IOMNPs into polymeric matrix [15]. In former case, the IOMNPs remained as an individual particle, whereas in later scenario, the particles are artificially coagulated into loosely packed polymeric matrix. Nevertheless, in all these cases the IOMNPs retained both its magnetic and catalytic properties, which are crucial for environmental engineering related application. In this article, we proposed the assembly of IOMNPs with layer-by-layer approach [16] onto silica colloid which served as nanotemplate and use this nanostructure for water treatment purpose. Cationic polyelectrolyte was employed as binding agent to promote the attachment of IOMNPs onto the silica colloid. The final nanocomposite composed of silica colloid as the inner core coated with polyelectrolyte and IOMNPs as outer-shell.

There present numerous chemical routes for the synthesis and surface modification of silica colloid and all these aspects contribute to the versatile use of silica colloid for engineering applications [17]. Silica alone is widely used in water remediation [18,19] where it served as adsorbent to remove Basic Blue 3 and Astrazone Blue(Basic) dyes respectively from textile effluent. Moreover, surface functionalization of silica colloid by decorating its micro or meso-porous channels and/or the external particle surface with various functional groups has significantly enhanced its effectiveness for environmental application [20,21]. Combining silica colloid and IOMNPs into one unified nanostructure offers attractive architecture for water remediation. Silica is widely chosen as material to functionalize IOMNPs due to its stability, possible reuse and relative rapidity in reaching equilibrium, high mechanical resistance and high surface area [22]. Deposition of silica shells on IOMNPs has been successfully carried out by different procedures [23,24]. On the other hand, embedding IOMNPs into silica matrix for wastewater treatment by taking advantage of its high surface areas and pore volumes has also being developed [13]. But the direct deposition of iron compounds on silica template is much more difficult [25]. There were some studies about the method of repetitive heterocoagulation to synthesize composite of silica core-repetitive magnetic/silica-shell [26] and developing Fe_3O_4 nanoparticle/polyelectrolyte multilayer assembly on colloidal silica [27].

Even though the design and synthesis of silica-core with magnetic-shell composite has been widely discussed in literature, to best of our knowledge, there are no any illustrations about the environmental engineering application of this composite material. There are several advantages to incorporate the IOMNPs onto silica colloid. Firstly, due to the cooperative nature of the magnetophoresis [28,29], these nanocomposite should be less susceptible to the thermal randomization energy compared to individual particle [30] and experienced much greater magnetophoretic force to overcome the viscous drag [31,32]. These scenarios would enable rapid magnetic collection of nanocomposite which composed of magnetic particles clusters after their usages for water remediation. Furthermore, the confinement of IOMNPs onto the surface of silica colloid mitigates the particles aggregation problems and also reduces the direct exposure of IOMNPs to environment. Thus, lessen the nanotoxicity of IOMNPs associated to its small dimension [33]. In addition, since the IOMNPs are artificially immobilized onto the silica colloid with loosely bound polyelectrolyte matrix, we anticipated that the deprivation of catalytic active sites of IOMNPs can be minimized. Subsequently, this open matrix structure allows the full utilization of catalytic capability of the nanocomposite formed for degradation of targeted pollutants.

In this work, positively charged Methylene Blue (MB) and negatively charged Methyl Orange (MO) dyes are chosen as modeled pollutants to test the aptitude of our as-synthesized silica colloid–polyelectrolyte–iron oxide composite for water remediation. In addition to ease of detection by colorimetric method, both MB and MO were selected as our model system due to their similarity in molecular structure (Fig. 1) and, obvious charge differences. By having very similar molecular structure, both MB and MO molecules would have comparable transportation behaviors. This feature allowed us to neglect the differences associated to their transport properties while comparing separation efficiency of these molecules in our dye removal experiments. Whereas, the charge differences between MB and MO provide us a unique opportunity to test the critical role of electrostatic interactions for pollutant removal by the silica colloid–polyelectrolyte–iron oxide composite via adsorption and catalytic degradation. We anticipated that electrostatic interaction would have much adverse effect on the former mechanism and is less influential on the latter case. In addition, MB and/or MO have been widely used in textile, printing, food, and pharmaceutical industries [34,35], and hence, industrial effluents containing these molecules need to be treated effectively to prevent further deterioration of our water resources. By investigating the feasibility of synthesized nanoparticles in dyes removal, the degradation of other organic pollutants from contaminated water can be readily carried out by using advanced oxidation process in this heterogeneous catalytic reaction system. In fact, the advanced oxidation process [36] is a promising method which has been used in various emerging heterogeneous Fenton system to treat contaminants in wastewater, for example colorants [37–40], herbicide [41], insecticide [42] as well as pharmaceutical waste [43,44].

2. Materials and methods

2.1. Materials

All the reagents employed in this work were of analytical grade and used as received without further purification. Ethanol

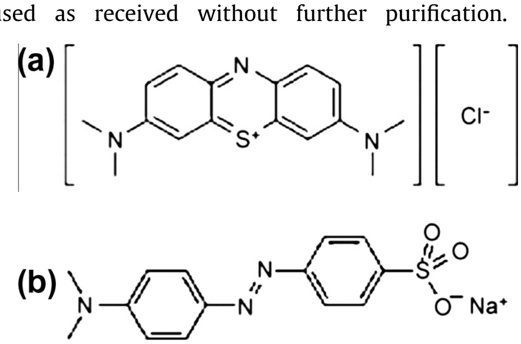

Fig. 1. The structural formula for (a) positively charged Methylene Blue (MB) and (b) negatively charged Methyl Orange (MO).