UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Design, Preparation and Characterization of Nanostructured Magnetic Colloid Augmented Polymeric Membrane for Underground Water Remediation

by
Dr. Lim Jit Kang
Prof. Abdul Latif Ahmad
Dr. Ooi Boon Seng

2012

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

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Dr. Ooi Boon Seng

4. **Tajuk Projek:** *Title of Project* Design, preparation and characterization of nanostructured magnetic colloid Augmented polymeric membrane for underground water remediation.

5. **Ringkasan Penilaian**/*Summary of Assessment*:	Tidak Mencukupi *Inadequate* 1	2	Boleh Diterima *Acceptable* 3	Sangat Baik *Very Good* 4	5
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☑	☐
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☑	☐
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☑	☐
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☑	☐	☐
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☐	☑	☐
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☑	☐

6. **Abstrak Penyelidikan**
(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**. Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research
(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Please refer to the attached file for full abstract in English and in Bahasa Melayu.

7. **Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini. [Sila gunakan kertas berasingan]**
Applicant are required to prepare a Comprehensive Technical Report explaining the project. (This report must be appended separately)

Please refer to attached document for the technical report.

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Magnet Koloid	Magnetic colloid
Rawatan Air	Water Treatment
Microcapsule polimer	Polymeric Microcapsule

8. **Output dan Faedah Projek**
Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

LiPeng Kong, XueJing Gan, Abdul Latif bin Ahmad, Bassim H. Hameed, Eric R. Evarts, BoonSeng Ooi, JitKang Lim, Design and synthesis of magnetic nanoparticles augmented microcapsule with catalytic and magnetic bifunctionalities for dye removal, Chemical Engineering Journal 197 (2012) 350 – 358.

(b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

Two high school students from Maktab Rendah Sains Mara Taiping, namely Fatin Najiha bt rahman and Atrah Adlin bt Ahmad Rizal, have involved in this project and learned critical issues regarding water pollution and how the nanotechnology can be implemented for underground water treatment. The data collected by the students were presented as their scientific project. In addition based upon the finding of this project the PI has also obtained one international grant from Nippon Sheet Glass Foundation.

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(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

Kong Li Peng, Sarjana Sains (Kejuruteraan Kimia) Penuh Masa, in progress

ii) Lain-lain:
Others
Gan Xue Jing, Final Year Project, Completed
Kong Li Peng, Final Year Project, Completed
Soo Kee Xian, Reseearch Assistant, Completed

9. **Peralatan yang Telah Dibeli:**
Equipment that has been purchased

Finnpipette F2 GLP Kit – micropipette.

Dr. Lim Jit Kang
Senior Lecturer
School of Chemical Engineering
Universiti Sains Malaysia

Tandatangan Penyelidik
Signature of Researcher

Sept 01, 2012
Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

This research project has been successfully completed.

**TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT**
*Signature of Chairman
[Research Committee of School/Centre]*

PROFESSOR AZLINA HARUN @ KAMARUDDIN
Dean
School of Chemical Engineering
Engineering Campus
Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
Penang, MALAYSIA.

6/9/12

Tarikh
Date

Abstrak Penyelidikan

Dalam projek ini, kita telah berjaya sintesis membran yang berstruktur kapsul dengan penambahan nanopartikel magnet (MNPs) ke dalam rangkaian tiga dimensi polimer. Microcapsule ini mempamerkan dua sifat unik, iaitu sebagai pemangkin dan bermagnetik. Kita telah berjaya menggunakan struktur ini bagi tujuan penyingkiran pencemar organik biru metilena (MB) dan arsenik daripada sumber air. Dua prinsip yang terlibat untuk proses penyingkiran bahan pencemar yang disebutkan di atas adalah terutamanya didorong oleh penyebaran dan tindak balas bermangkin. Penjerapan didorong oleh penyebaran bahan pencemar dalaman melalui rangkaian polimer adalah bertanggungjawab untuk penyingkiran bahan pencemar pesat jika microcapsule baru disintesis telah bekerja. Manakala untuk microcapusule kitar semula, degradasi pemangkin adalah mekanisme penyingkiran utama. Saintifik, kita telah menekankan kesan kompetitif interaksi elektrostatik antara pencemar dan MNPs dengan kestabilan koloid MNPs dalam menetapkan keupayaan degradasi pemangkin microcapsule. Kami mendapati bahawa kestabilan koloid adalah lebih penting daripada sumbangan interaksi elektrostatik dalam menetapkan penyingkiran pencemar sekiranya polyelectrolyte dengan berat molekul rendah digunakan.

Abstract of Research

In this project, we have successfully synthesized capsule-liked membrane structure with incorporation of magnetic nanoparticles (MNPs) into three dimensional polymeric networks. This microcapsule exhibited both catalytic and magnetic properties. We have managed to employ this nanostructure for the removal of organic pollutant - methylene blue (MB) and heavy metal - arsenic from water resources. The two working principles involved for aforementioned pollutants removal process are mainly driven by diffusion and catalytic reaction. Adsorption driven by inner diffusion of pollutants through the polymeric network is responsible for the rapid removal of the pollutants if the freshly synthesized microcapsule was employed. Whereas for the recycled microcapusule, catalytic degradation is the main removal mechanism. Scientifically, we have highlighted the competitive effect of electrostatic interactions between the pollutant and MNPs with colloidal stability of MNPs in dictating the catalytic degradation capability of microcapsule. We found that colloidal stability superseded the electrostatic interaction contribution in dictating the pollutant removal if low molecular weight of polyelectrolyte is employed.

Applicant are required to prepare a Comprehensive Technical Report explaining the project. (This report must be appended separately)

In this project we have successfully integrated spherical and rod-liked Fe^0/iron oxides nanoparticles (see Fig. 1) into Polyvinylidene Fluoride (PVDF) polymeric microcapsule via phase inversion technique (see Fig. 2). This synthesis technique allows the encapsulation of Fe^0/iron oxides nanoparticles, with both magnetic and catalytic properties, into PVDF polymeric microcapsule which further enhances its pollutant removal efficiency through two mechanisms: adsorption by polymeric network, follow with catalytic degradation by nanoparticles. Here we fabricate the membrane in spherical capsule form rather than conventional flat sheet membrane due to (1) the ease of releasing this structure into soil environment and (2) manipulating it by externally applied magnetic field.

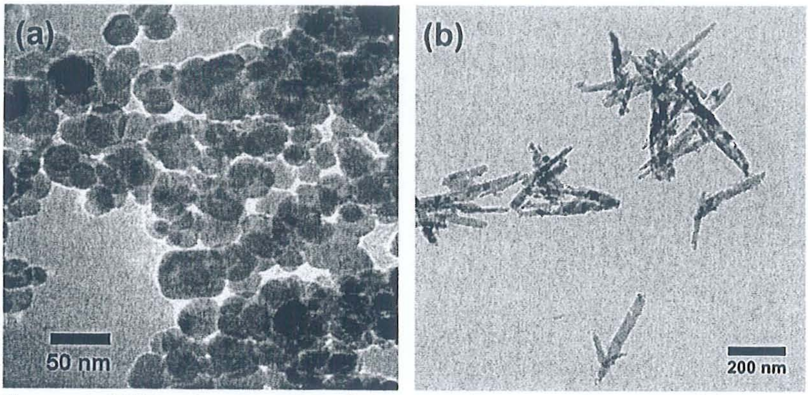

Figure 1. TEM micrographs of NPs employed in this study (a) Sigma nanospheres, and, (b) TODA nanorods.

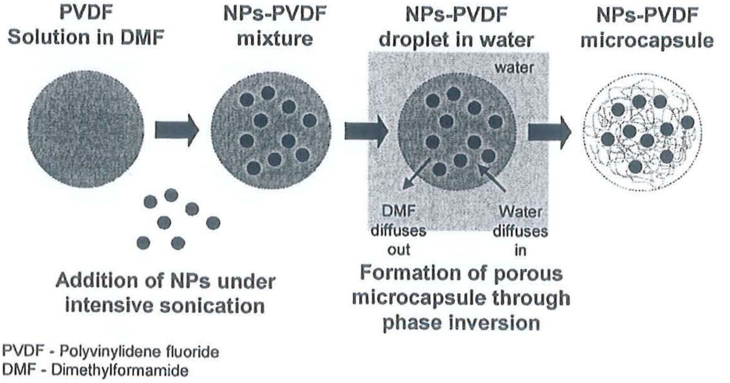

Figure 2. Pictorial representation showing the steps involved in phase inversion technique to synthesize magnetic nanoparticles augmented PVDF microcapsule.

To form a colloidally stable nanoparticle suspension, we surface functionalized our magnetic nanoparticles with Poly(diallydimethylammonium) Chloride (PDADMAC). This surface functionalization procedure was applied to the all PDADMAC with different molecular weight. Malvern Zetasizer Nano ZS was employed to perform Dynamic Light Scattering (DLS) and electrophoretic mobility measurement to verify the successful attachment of PDADMAC onto the surfaces of NPs (see table 1). Besides, DLS was also used to determine the particle size distribution in term of hydrodynamic diameters. The light scattering intensity autocorrelation function was fitted by the CONTIN algorithm to produce an intensity-weighted distribution of hydrodynamic radii. DLS analysis provides a way to monitor the colloid stability of the nanospheres and nanorods before and after the attachment of PDADMAC. These surface functionalized particles would later on introduce into polymeric solution and subsequently forming microcapsule (see Fig. 3).

As for the comparison between the nanorod and nanosphere PVDF microcapsules is concerned, nanospheres tend to form smaller clusters scattered all over the internal surface of microcapsules with each cluster composed of limited number of individual nanospheres (Fig. 3d). The extent of agglomeration that leads to the formation of NP clusters, however, is not that severe compared to the case of nanorods. This condition is mainly due to the existence of poly(vinyl pyrrolidone) layer that serves as the steric barrier around the Sigma nanosphere. Nevertheless, this result gives a strong indication suggesting the need for surface functionalization of the NPs prior to their encapsulation into PVDF-network. This step will increase the surface-to-volume ratio of NP, with respect to the microcapsule, that is needed to fully realize its potential for catalytic degradation of targeted pollutant(s).

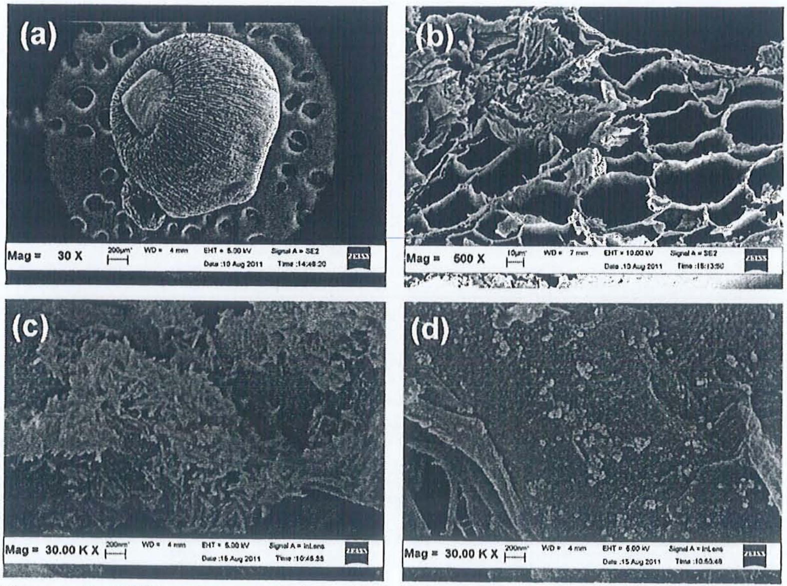

Figure 3. SEM micrographs of synthesized microcapsules (a) entire species of PVDF microcapsule under low magnification showing its outer surface is occupied with small opening, (b) internal porous structure of PVDF microcapsule, (c) internal structure of nanorods-PVDF microcapsule with its inner wall fully covered by nanorod aggregates, and (d) internal structure of nanospheres-PVDF microcapsule with small nanosphere clusters scattered around the inner surfaces.

By having the magnetic nanoparticles within the PVDF microcapsule has at least boost the capability to remove organic pollutant by a factor of three compared to freely suspended nanoparticles (see Fig. 4) and recorded a removal efficiency of ~80 mg/g-microcapsule. After subjected to five cycles of pollutant removal, the nanoparticle augmented microcapsules are still retaining more than ~90 % of their initial performance while the PVDF-only microcapsule loses its removal capability after the first cycle.

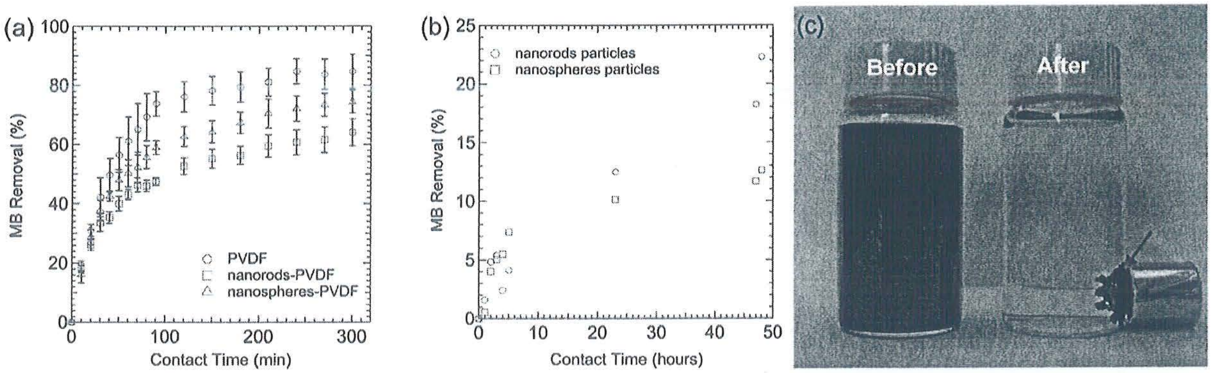

Figure 4. The comparison of MB removal efficiency by using (a) three types of freshly synthesized microcapsules, and (b) the dispersion of nanorods, and nanospheres particles only. For MB degradation processes upto 24 hours by using NPs-microcapsule have resulted total removal percent of 94% for PVDF, 86% for nanospheres-PVDF microcapsules, and 70% for nanorods-PVDF microcapsules. (c) The discolourization of MB caused significant color transition from initial dark blue (100ppm) to light blue. The arrow indicates the collected NPs-PVDF microcapsules.

In addition to organic dye, we have also tested the capability of using this composite nanomaterial for heavy metal – arsenic removal (Fig. 5). In contrast to methylene blue removal, in which catalytic degradation through Fenton- and Fenton-like reaction play a significant role, the arsenic removal by this structure is mainly adsorption driven. However, the attachment of the arsenic onto the iron-based nanoparticles is a much complicated process and involved surface binding complex formation. There are ample evidences suggesting that the arsenic adsorption onto iron oxide surfaces is through inner sphere complex formation and the true mechanism and underlying detail of this complex formation is the main subject of our study in future.

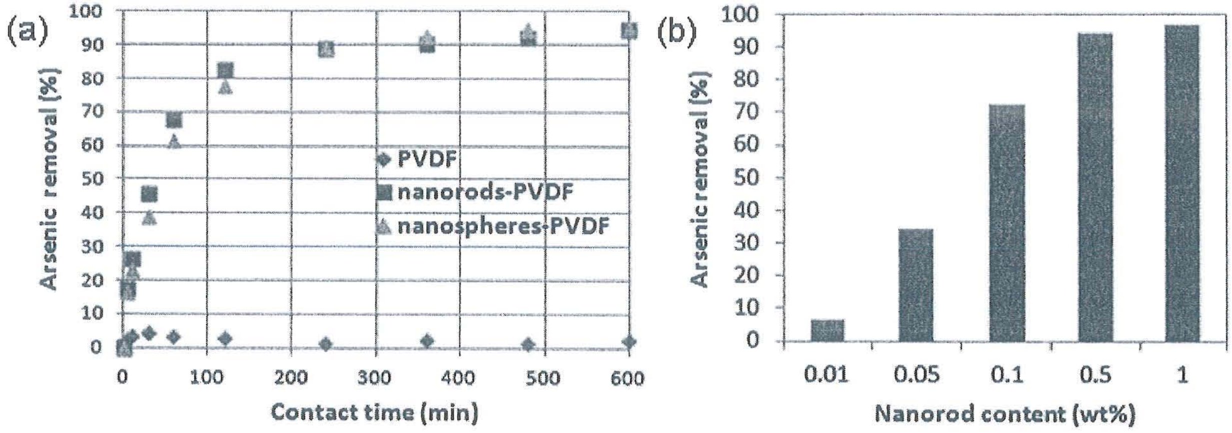

Figure 5. Arsenic removal by using (a) three types of freshly synthesized microcapsules, and (b) by varying the iron oxide content of microcapsule employed.

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Design and synthesis of magnetic nanoparticles augmented microcapsule with catalytic and magnetic bifunctionalities for dye removal

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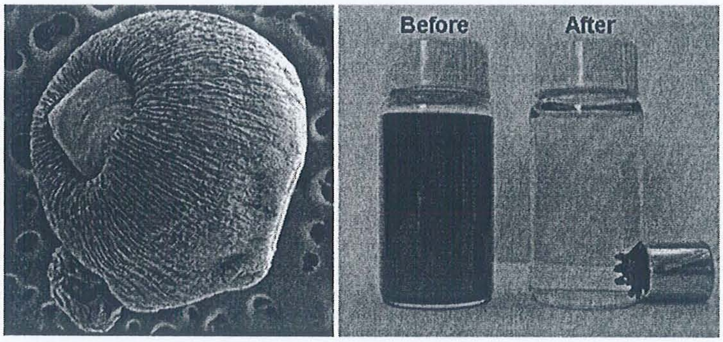
HIGHLIGHTS

- Synthesis of nanoparticles–polymeric microcapsule by phase inversion technique.
- Hybrid materials with catalytic and magnetic properties.
- The as synthesized microcapsule achieved high methylene blue loading at 80 mg/g.
- After recycled for five times the microcapsule still retained >90% initial efficiency.
- Colloid stability and electrostatic interaction contributions were investigated.

GRAPHICAL ABSTRACT

Magnetic nanoparticle augmented polymeric microcapsule with magnetic and catalytic bifunctionalities can be employed for decolorization of methylene blue.



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ABSTRACT

Here we describe the integration of spherical and rod-liked Fe^0/iron oxides nanoparticles into polyvinylidene fluoride (PVDF) polymeric microcapsule via phase inversion technique. This synthesis technique allows the encapsulation of Fe^0/iron oxides nanoparticles, with both magnetic and catalytic properties, into PVDF polymeric microcapsule which further enhances its pollutant removal efficiency through two mechanisms: entrapment by polymeric network, follow with catalytic degradation by nanoparticles. A model system by using methylene blue (MB) as targeted pollutant was employed to test the feasibility of this idea. By having the magnetic nanoparticles within the PVDF microcapsule has at least boost the capability to remove MB by a factor of three compared to freely suspended nanoparticles and recorded a removal efficiency of ~80 mg/g-microcapsule. After subjected to five cycles of MB removal, the nanoparticle augmented microcapsules are still retaining more than ~90% of their initial performance while the PVDF-only microcapsule loses its MB removal capability after the first cycle. The successful surface functionalization of magnetic nanoparticles was characterized by dynamic light scattering (DLS) and electrophoretic mobility measurement. The effects of surface functionalization of magnetic nanoparticles on the MB removal are interpreted in terms of the particle-pollutant electrostatic interaction, and the colloidal stability of the particles before its encapsulation into the polymeric network. Both nanorod-PVDF and nanosphere-PVDF microcapsules retained their magnetic properties after MB removal and can be magnetophoretically collected in real time by a permanent NdFeB magnet with surface magnetic field at approximately 5500 gauss.

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1. Introduction

In recent years magnetic nanoparticles (NPs) with sizes ranging from 1 to 100 nm have attracted much interest in many environmental engineering related applications mainly due to its ability to serve as nanosorbents [1] for pollutant removal from water resources [2]. Nano-sized particles with high surface-to-volume ratio, and hence, high loading capacity, has making it an ideal candidate as nanoagent to remove pollutants such as trichloroethylene (TCE) [3], arsenic [4] and heavy metals [5], organic waste [6] and dye [7] out from water resources. As for the realization of engineering applications of the magnetic NPs is concerned, the strong adsorptive behavior of dye molecules onto iron oxide nanocrystalline surface [8], together with their catalytic [6] and magnetic [2] properties, placed them in an advantageous position to clean dye contaminated water.

Large amount of dye contents found in the disposed effluents of textile, paper, leather, cosmetics industries, upon mixing with the water bodies, would cause severe environmental and health problems. As these dyes are being released into water, they undergo chemical as well as biological changes [9], increasing the chemical oxygen demand (COD) and reducing light penetration and visibility [10]. Furthermore, certain dyes and its degradation counterparts are potentially carcinogenic and toxic [11], and hence, their presence in water poses serious threats to aquatic life and human populations. Thus, water pollution issues originated from industrial dye-laden effluents need to be addressed effectively to prevent further deterioration of water resources.

To benefit from the aforementioned unique features of magnetic NPs for dye removal from water, most of the strategy proposed to date, such as the one suggested by Saha and coworkers [8], are relying on the initial exposure of pollutant (various dyes containing hydroxyl group as for Saha's case) to freely suspended NPs follows with the recollection of the particles by an externally applied magnetic field. Since the magnetophoretic forces experienced by the NPs are proportional to their volume (see Eq. (1)) [12], hence, the re-collection of the freely suspended nanoparticles is extremely difficult as ultra-large magnetic field gradient ∇B is required to generate high F_{mag} to overcome the thermal randomization energy originated from the Brownian motion of the particles [13]. This limitation makes direct collection of NPs less attractive.

$$F_{mag} = \frac{V_m \Delta\chi}{\mu_0}(B \cdot \nabla)B \tag{1}$$

In addition, more evidences have recently surfaced indicating the risk of (eco)toxicological impacts of nanomaterials [14]. The contributing factors of nanotoxicity are still subjected to debate; however, it is very likely due to the characteristic small dimensional effects of nanomaterials that are not shared by its non-nanoscale counterparts with the same chemical composition [15], or, biophysicochemical interations at the nano-biointerface dictated by colloidal forces [16]. For either reason, the release of great amount of NPs without surface functionalization to environment should be avoided.

In the present study, we propose the usage of magnetic NPs-polymeric microcapsule for dye removal from water resources. The encapsulation of the NPs within polymeric network would drastically reduce the risk associated to the nanotoxicity as the direct physical contact of the NPs to its surrounding is minimal. In addition, the polymeric matrix acts as a barrier to localize the magnetic nanoparticles (acting as a catalyst) and pollutants in confined space, which subsequently would improve their physical contact and promote the catalytic degradation of pollutants [17]. Furthermore, the microcapsules prepared would also exhibit better catalytic stability and recyclability without loss of activity after multiple cycles of catalytic degradation runs [18]. Due to the collective magnetophoretic forces experienced by all the trapped NPs, we anticipated that this hybrid material would response much rapidly even at very low magnetic field gradient compared to individual particle.

Here methylene blue (MB) is chosen as the modeled pollutant to test the feasibility of our idea due to its ease of detection by colorimetric method. Two commercially available Fe^0/iron oxides nanorods from TODA America and nanosphere from Sigma Aldrich (Fig. 1) were encapsulated into three dimensional polyvinilydene fluoride (PVDF) polymeric networks to form microcapsule by using phase inversion technique (Fig. 2) [19]. We used these two species of magnetic nanoparticles because of their differences in (i) magnetophoretic behavior [13,20], (ii) dispersibility of the particle suspension formed as rod-like magnetic nanoparticles has higher tendency to aggregate than spherical particles, so, the colloidal stability effects on MB removal can be tested, and also (iii) their availability in large quantity which is crucial for the engineering applications of nanomaterials. Whereas PVDF is used as base polymer for the construction of microcapsule due to advantages such as high purity, high mechanical strength and its high chemical, pH and heat resistance [21].

Entrapment of Fe^0/iron oxides NPs into the PVDF-polymeric network allows us to integrate the magnetic and catalytic characteristics of Fe^0/iron oxides NPs into a macroscopic porous structure. With these two materials, namely Fe^0/iron oxides NPs and PVDF polymeric network, integrated into single entity would further enhance the dye removal efficiency as it capable to remove targeted MB through two mechanisms: entrapment of MB by polymeric network, follow by catalytic degradation through Fenton and Fenton-like reaction [22]. Moreover, having magnetic NP clusters within this structure has significantly increase its magnetophoretic responsiveness by several orders of magnitude [23], hence, enables the real time collection and recycling of these microcapsule for environmental engineering applications.

2. Materials and Methods

2.1. Materials

Polyvinylidene fluoride (PVDF) was purchased from Solef, Solvay Solexis. Dimethylformamide (DMF), hydrogen peroxide (35 wt.% in water) and methylene blue (MB) (M_w = 319.8) was obtained from Merck. The Fe^0/iron oxides nanosphere (with hydrodynamic diameter ~20 nm) and nanorods (with length ~300 nm and diameter ~20 nm) [20] were supplied by Sigma Aldrich and TODA America, respectively (Fig. 1). Alternating gradient magnetometry [20] and vibrating sample magnetometry (conducted by ARkival Technology Corp., USA) measurements were performed at room temperature on a know amount of TODA nanorod and Sigma nanospheres and the specific magnetization of the particles were revealed at ~90 emu/g and 70.4 emu/g, respectively. Sodium dodecyl sulfate SDS (95% based on total alkyl sulfate content) and poly(diallyldimethylammonium chloride) (PDADMAC) with Avg. molecular weight $M_w < 100{,}000$ (very low molecular weight), $M_w \sim 100{,}000–200{,}000$ (low molecular weight), $M_w \sim 200{,}000–350{,}000$ (medium molecular weight) and $M_w \sim 400{,}000–500{,}000$ (high molecular weight) were purchased from Sigma Aldrich. In all experiments, deionized water employed was produced by using Purelab Option-Q with resistivity up to 18.2 MΩ cm from a potable water source. All the chemicals were of analytical grade and used without further purification or treatment.

2.2. Preparation of PVDF solution

Initially, 10 g of PVDF powder was added into a beaker containing 90 g of DMF solvent with the sensor tip of thermometer immersed into it. After the addition of PVDF powder, this mixture was sealed with parafilm instantaneously while subjecting to

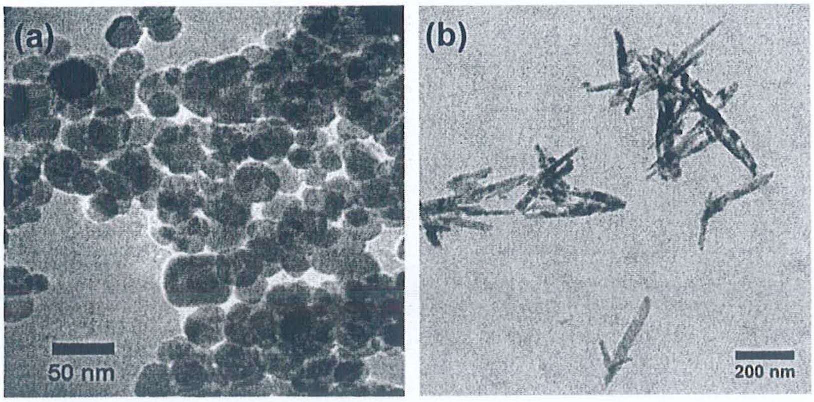

Fig. 1. TEM micrographs of NPs employed in this study (a) Sigma nanospheres and (b) TODA nanorods.

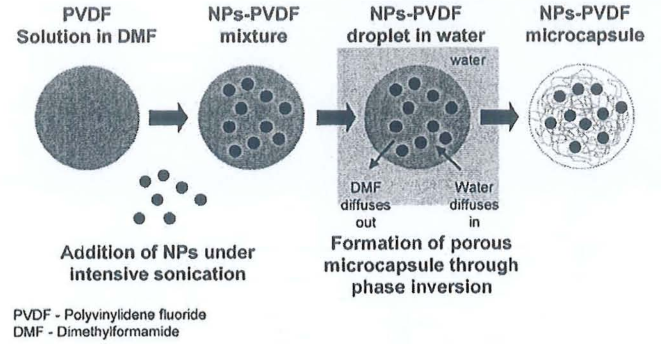

Fig. 2. Pictorial representation showing the steps involved in phase inversion technique to synthesize magnetic nanoparticles augmented PVDF microcapsule.

constant stirring at 180 rpm. This mixture was then heated from room temperature to 65 °C with a heating rate at 10 °C/min and was left under this condition with continuous heating for 70 min. Immediately after this step, the solution was cooled to 40 °C and was left for overnight under constant stirring.

2.3. Preparation of Fe^0/iron oxides nanoparticles-PVDF solution

The NPs-PVDF solution was prepared by the addition of 0.30 g of nanoparticles into 60 g of polymer solution but not vice versa. The mixture had a particle concentration of ~0.5 wt.%. In order to ensure full dispersion of NPs, direct addition of NP powder into the PVDF solution should be avoided. Here we first dispersed the full amount of NPs into 10 g of PVDF solution contained insides a 20 mL glass valve under intensive sonication for at least 10 min. This well-mixed NPs-PVDF solution was then slowly added into the remaining PVDF solution under sonication. All these steps are necessary to ensure the uniform distribution of nanoparticles insides the polymeric solution. The morphology of TODA nanorods and Sigma nanospheres employed in this research was analyzed by Phillips CM12 Transmission Electron Microscope (TEM) with Docu Version 3.2 image analysis software (Fig. 1). The elemental composition of the TODA nanorods and Sigma nanospheres was determined by X-ray diffraction (Bruker Axs D8 Advance) in a range of diffraction angle from 0° to 90° of 2θ.

2.4. Surface functionalization of Fe^0/iron oxides nanoparticles with very low molecular weight of poly(diallydimethylammonium) chloride (PDADMAC)

To form a colloidally stable nanoparticle suspension, we surface functionalized our magnetic nanoparticles with PDADMAC. A total of 400 µL of PDADMAC, 35 wt.% in H_2O, was pipetted into a beaker containing 200 mL of deionized water (DI) and left for at least 24 h for full dissolution. A particles solution at the concentration of 1.5 g/L was prepared by adding 0.30 g of nanoparticles into 200 mL of DI water. Both as-made solutions were then mixed together by drop-wise addition of nanoparticle suspension into PDADMAC solution while subjecting to intermittent sonication. Later on, the surface functionalized nanosphere was collected by using a NdFeB permanent magnet and kept inside oven for drying and to remove water residue. This surface functionalization procedure was applied to the all PDADMAC with different molecular weight. Malvern Zetasizer Nano ZS was employed to perform dynamic light scattering (DLS) and electrophoretic mobility measurement to verify the successful attachment of PDADMAC onto the surfaces of NPs (see Table 1). Besides, DLS was also used to determine the particle size distribution in term of hydrodynamic diameters. The light scattering intensity autocorrelation function was fitted by the CONTIN algorithm to produce an intensity-weighted distribution of hydrodynamic radii. DLS analysis provides a way to monitor the colloid stability of the nanospheres and nanorods before and after the attachment of PDADMAC. For nanorods, the measured hydrodynamic radius is estimated based upon the equivalent sphere approximation [24].

2.5. Synthesis of Fe^0/iron oxides nanoparticles-PVDF microcapsules

The experimental setup for the preparation of Fe^0/iron oxides nanoparticles-PVDF microcapsules is illustrated in Fig. 3. PVDF solution was channeled through a micropipette tip at the pumping speed of around 0.5 mL/min by Watson Marlow Peristaltic Pump followed by drop-wise addition of this polymer solution into a coagulation bath composed of 0.5 wt.% sodium dodecyl sulfate (SDS) in DI water for microcapsules formation. The position of coagulation bath was adjusted manually to avoid the accumulation of microcapsules formed in one single area. Having too many polymeric microcapsules undergoing phase inversion process in one region will promote the fusion of multiple microcapsules together to form doublet, triplet or even a clump of large polymeric clusters. This method was applied to synthesize all three types of microcapsules employed in this study. Fe^0/iron oxides NPs-PVDF solution was sonicated before the synthesis to promote better dispersion of NPs within the polymer solution which subsequently leading to uniform distribution of NPs within the polymeric matrix formed. The internal structure and the overall morphology of microcapsules formed were studied by ZEISS Supra 55 VP Scanning Electron Microscope (SEM) imaging (Fig. 4).

To determine the porosity of the microcapsules formed, we employed the water-to-mass ratio measurement as follow. The weight of water entrapped into the internal pores of microcapsules was determined by heating them mildly inside an oven under 59.7–60.3 °C and a cabinet under room temperature as controlled sample, respectively. Those microcapsules in oven were weighted for first 2 h with 5 min interval between the measurements and were left for overnight; after that, the same samples were weighted again at 30 min interval of time for 5 h. The same procedure was carried out for samples in cabinet. Both of the samples had been left overnight again after taking the readings for 5 h at 30 min interval, and the weight data obtained were higher than the former one. This result showed that microcapsules shrunk after over exposure to the air where no molecular water to support the internal structure of microcapsules; hence, the volume of microcapsules decreased leading to the increase of density. This experiment was carried out at the same time for PVDF, 0.5 wt.% nanorods-PVDF, 0.5 wt.% nanospheres-PVDF microcapsules in order to apply a consistent environmental condition for accurate comparison among them.

2.6. Degradation tests of MB

The MB degradation experiments were carried out in triplicate with the model system composed of 100 mL MB solution at the concentration of 100 ppm. Moreover, 5 mL of H_2O_2 was added as electron donor [25]. Here the initial concentration of MB is set at 100 ppm to make sure the complete saturation of all the available sorption sites within the microcapsule, and hence, its catalytic property can be tested. These experiments were conducted at room temperature and the colorimetric measurement was initiated right after the addition of 0.5 g of microcapsules into MB solution under vigorous stirring at 350 rpm. In order to illustrate the reusability of the NPs augmented microcapsule for discoloration of MB through Fenton and Fenton-like reaction, after the first MB degradation test, these microcapsules were recollected back by using a cylindrical NdFeB magnet and were subjected to next cycle of MB removal with same experimental procedure. The total amount of MB removed was determined via solution depletion technique by spectrophometrically recorded the absorbance spectra of remaining MB in the solution. For this purpose, Shidmazu UV-1601 UV–vis spectrophotometer was employed to analyze the MB concentration at the wavelength of 666 nm corresponded to the maximum molar extinction coefficient of MB [26].

3. Results and discussion

3.1. Microcapsule characterization

The microcapsule showed a satisfactorily spherical appearance as shown by SEM analysis of Fig. 4, and the averaged diameter of PVDF, nanorods-PVDF, and nanospheres-PVDF microcapsules measured over 100 samples for each sample were 1.845 ± 0.005 mm, 1.845 ± 0.007 mm, and 1.800 ± 0.006 mm, respectively. These values were very close to the size of the PVDF microcapsule synthesized through well-established non-solvent induced phase inversion method at ~1.3 mm [18]. The overall structure and size of microcapsule formed is normally depend on the type of solution, amount of SDS surfactant used, diameter of micropipette tip as well as the distance between micropipette tip and surface of coagulation bath. Only under well controlled experiment the spherical structure can be obtained.

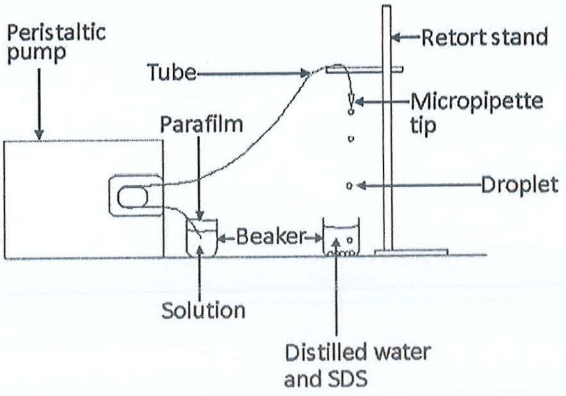

Fig. 3. Schematic diagram of experimental setup during synthesis of different types of microcapsules.

As depicted in Fig. 4b–d, all three species of microcapsules possess very similar porous internal structure, suggesting the formation of three dimensional polymeric network, regardless the presence of NPs. This characteristic porous-structure of microcapsules makes the entrapment of MB molecules via diffusion possible with existing concentration gradient across the outer layer of microcapsule as main driving force for this process to happen. After the entrapment of MB molecular in the polymeric voids, these molecules adsorbed onto the internal surface of polymer matrix, or/and, undergoing Fenton and Fenton-like reaction catalyzed by Fe^0/iron oxides NPs. However, the aggregation of nanorods (Fig. 4c) onto the internal surface of PVDF microcapsules, mainly due to the magnetic shape anisotropy effects [27], suggested the need to functionalize the surface of nanorods in order to form a stable NPs dispersion which will lead to more uniform distribution of this particle into the PVDF matrix.

As for the comparison between the nanorod and nanosphere PVDF microcapsules is concerned, nanospheres tend to form smaller clusters scattered all over the internal surface of microcapsules with each cluster composed of limited number of individual nanospheres (Fig. 4d). The extent of agglomeration that leads to the formation of NP clusters, however, is not that severe compared to the case of nanorods. This condition is mainly due to the existence of poly(vinyl pyrrolidone) layer that serves as the steric barrier around the Sigma nanosphere. Nevertheless, this result gives a strong indication suggesting the need for surface functionalization of the NPs prior to their encapsulation into PVDF-network. This step will increase the surface-to-volume ratio of NP, with respect to the microcapsule, that is needed to fully realize its potential for catalytic degradation of MB.

Table 1
Zeta potential and average hydrodynamic diameter of nanorods and nanospheres before and after surface functionalized by PDADMAC. The error bars represent the standard deviation of the measurements.

Surface functionalization	Nanosphere		Nanorod	
	Before	After	Before	After
Zeta potential (mV)	−30.0 ± 0.4	+55.1 ± 0.9	−29.4 ± 0.2	+43.4 ± 0.3
Ave. Hydrodynamic Diameter (nm)				
Very Low M_w PDADMAC	303.6 ± 8.5	383.2 ± 14.6	1075.4 ± 35.9	319.8 ± 3.3
Low M_w PDADMAC				382.1 ± 41.1
Medium M_w PDADMAC				1198.5 ± 177.3
High M_w PDADMAC				1677.4 ± 61.3

*Zeta potential measurements were performed on those nanoparticles surface functionalized by very low molecular weight PDADMAC only.

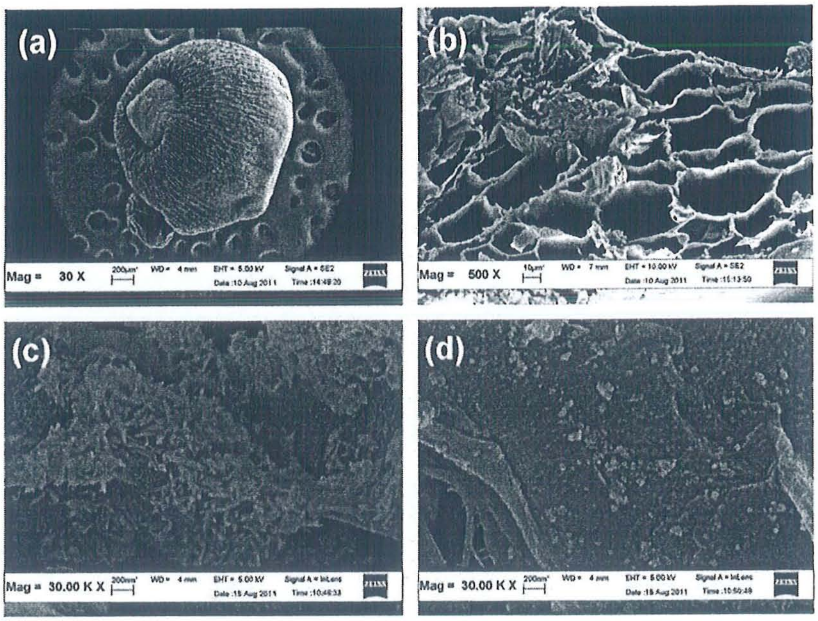

Fig. 4. SEM micrographs of synthesized microcapsules (a) entire species of PVDF microcapsule under low magnification showing its outer surface is occupied with small opening, (b) internal porous structure of PVDF microcapsule, (c) internal structure of nanorods-PVDF microcapsule with its inner wall fully covered by nanorod aggregates, and (d) internal structure of nanospheres-PVDF microcapsule with small nanosphere clusters scattered around the inner surfaces.

3.2. MB removal using freshly prepared microcapsules

As clearly depicted in Fig. 5a, the process of MB removal induced by all three types of microcapsules follow a similar trend with rapid initial uptake rate within the range of 0.09–0.22 mg/min and gradually reached a steady state for extended period. Similar behavior in dyes removal can be found in Rhizopus Arrhizus [28], Commercial Activated Carbon (CAC) [29], Polyacrylic Acid-bound Iron Oxide Magnetic NPs [9], Nanoporous SBA-3 [30] as well as Activated Carbon Derived from Agricultural Waste Material [31]. After the degradation of MB, the NPs augmented microcapsules still retained their magnetic properties and can be easily collected by a NdFeB permanent magnet with a surface magnetic field of ~5500 Gauss (Fig. 5c). The collection was rapid and instantaneous over a distance of few centimeters suggesting the strong magnetic coupling between the magnetic NPs residing within the PVDF microcapsule.

The average void volume of PVDF, nanorods-PVDF and nanospheres-PVDF microcapsules at room temperature is 0.45 cm^3/g, 0.48 cm^3/g, and 0.46 cm^3/g, respectively. In this work, all the PVDF solution prepared was based on the same weight percent of PVDF solution (10 wt.% PVDF powder in DMF solvent), and the void volume analysis shows that all three types of microcapsules having very similar internal void space to microcapsules weight irrespective to the presence of NPs. Since the porosity difference among these three microcapsules is negligible thus it cannot account for the variation witnessed in their capability to remove MB as illustrated in Fig. 5a. Here we hypothesized that there are two main factors contribute to the observation in Fig. 5a in which the fresh PVDF microcapsules out performed NPs-PVDF microcapsules. Firstly, the available surface area of PVDF matrix for MB adsorption plays an important role in this rate determining step. It is clearly shown in the SEM micrographs (Fig. 4c and d) that the nanorods and nanospheres randomly covered up certain portion of the internal surface area of PVDF matrix, hence, slightly reduced the available sites for MB adsorption. If this scenario is true, the total available internal surfaces to accommodate MB should be more in PVDF-only microcapsules compared to both nanospheres-PVDF and nanorods-PVDF microcapsules. This is the main reason for PVDF-only microcapsule out performed both nanospheres-PVDF and nanorods-PVDF microcapsules in MB removal. For freshly synthesized microcapsule, it is very likely that the electrostatic interaction between the MB molecules and the PVDF matrix plays a vital role in MB removal. PVDF is negatively charge due to its largest electronegativity of fluorine [32,33] which favorable attracted positively charged MB molecules [34]. After the adsorption, the Fenton and Fenton-like reactions would be the next immediate step contributes to the MB removal after its partitioning into the PVDF matrix. Fenton and Fenton-like reactions are well known as production methods of free hydroxyl radicals via the presence of Fe together with oxidants (e.g. H_2O_2) [35,36]. The produced free hydroxyl radicals ($^{\cdot}OH$) degrade the organic pollutants such as dyes by breaking the benzene ring [37,38] and relevant molecules in the structures to simple substances [39]. Hence, the successive adsorbed MB molecules on sorption sites are further degraded.

In addition, the colloid stability of NPs before their encapsulation into PVDF matrix has also played a pivotal role in determining the total MB removal efficiency of microcapsule employed. Due to the combinatorial effects of TODA nanorods containing higher amount of Fe^0 (Fig. 6) resulting stronger magnetic dipole–dipole interaction [40], together with its magnetic shape anisotropy [41] would eventually leading to higher magnetostatic interactions [42]. Under these circumstances, nanorods have more tendency to flocculate and forming large aggregates during the process of dispersion and formation of magnetic microcapsules. These closely packed nanorods would provide less catalytically active surfaces to initiate the Fenton/Fenton-like reaction for MB degradation. In addition, the localization of MB molecules entrapped within the PVDF matrix has greatly improved the near diffusion-limited rates of MB degradation process [43], compared to those freely suspended NPs (Fig. 5b), and this observation is consistent with the previous finding [44]. The descending order for total MB removal efficiency started with PVDF microcapsules, followed by nanospheres-PVDF and lastly nanorods-PVDF microcapsules (Fig. 5a), strongly supports this hypothesis.

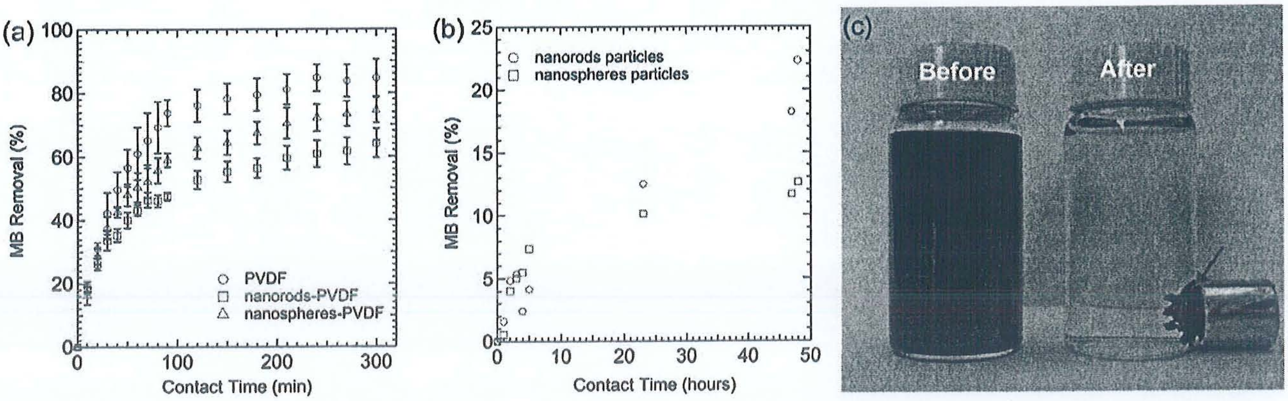

Fig. 5. The comparison of MB removal efficiency by using (a) three types of freshly synthesized microcapsules, and (b) the dispersion of nanorods, and nanospheres particles only. For MB degradation processes up to 24 h by using NPs-microcapsule have resulted total removal percent of 94% for PVDF, 86% for nanospheres-PVDF microcapsules, and 70% for nanorods-PVDF microcapsules. (c) The discolorization of MB caused significant color transition from initial dark blue (100 ppm) to light blue. The arrow indicates the collected NPs-PVDF microcapsules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

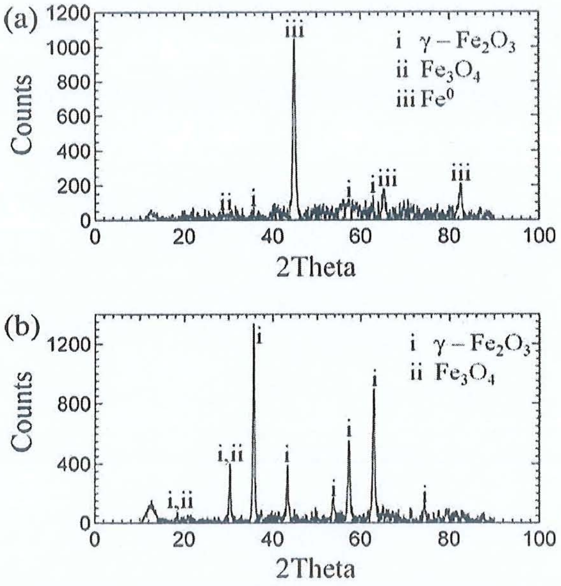

Fig. 6. XRD diffractogram of (a) TODA nanorods, and (b) Sigma nanospheres showing the elemental composition of the magnetic nanoparticles.

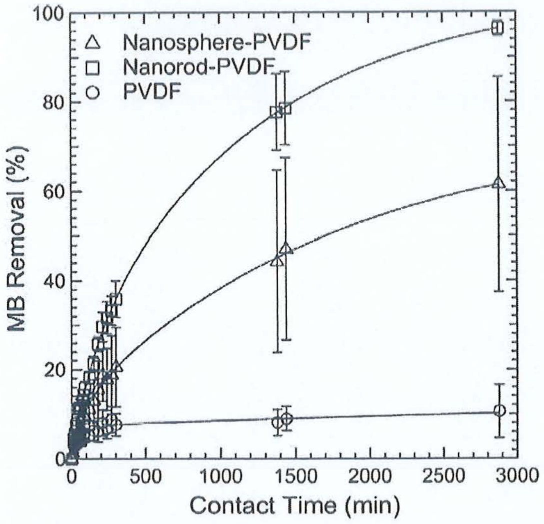

Fig. 7. Percent MB (with 100 ppm initial concentration) removal achieved by using recycled NPs-PVDF microcapsules.

3.3. Recycle use of nanoparticle–microcapsule for MB removal

A series of experiment was conducted to test the feasibility of using the synthesized microcapsules for multiple MB degradation cycles. The results obtained would also provide us with more detail information regarding the life span of these microcapsules for engineering applications without having NPs leached out from the PVDF matrix. In contrast to the performance of their freshly synthesized counterparts, which was discussed in previous section, recycled nanorods-PVDF microcapsule gives the highest MB removal efficiency (Fig. 7). Nanorods-PVDF microcapsules performed consistently in every regeneration cycles by achieving an average removal efficiency of ~95% after 2 days. On the other hand, the MB removal efficiency for nanospheres-PVDF microcapsules is approximately 61%. The discrepancy of these two results is attributed to the elemental composition difference of TODA nanorod and Sigma nanosphere. As clearly depicted in the diffractogram of both species of particles in Fig. 6 there are high percentage of zerovalent iron in nanorods, and maghemite in nanospheres, respectively. The presence of zerovalent iron and magnetite in the nanorods compounds promote the Fenton and Fenton-like reaction compared to the just pure magnetite [22] since favorable electron transfer promotes higher production of Fe^{2+}. In addition, Fenton reaction is much more rapid than Fenton-like reaction for the initial removal of dye [25] and this leads to the divergent performance for both nanorods and nanospheres in MB removal tests within the similar time frame. For PVDF microcapsules, in spite of prolonging its contact time with MB solution, it simply removed around 10% of initial MB amount. This is a clear indication showing that the Fenton and Fenton-like reaction (catalytic degradation) [43] dominating the recycling MB removal processes instead of the entrapment/adsorption mechanism driven by pure PVDF polymeric network. The total loading capacity for nanorods-PVDF microcapsules in our experiments is obtained at ~80 mg/g without fitting it with any isotherm. Its ranking in loading capacity compared to other nanoadsorbents generated from waste is tabulated in Table 2. As far as loading capacity is concerned, the NPs-PVDF microcapsule is at least as competent in removing azo dye from water resources. Removal efficiency as high as ~90% can still be achieved by nanorods-PVDF microcapsules even after gone through five completed cycles of MB removal.

Table 2
Comparison of the absolute loading capacity of nanorods-PVDF microcapsules used in this work to other nanosorbents [45].

Material	Loading capacity (mg/g)
Soy meal hull	114.94
AC-Charcoal	101
Nanorod-PVDF microcapsules (this work)	80
Chitosan/cyclodextrin material	77.4
Hazelnut shell	60.2
GAC Filtrasorb 400 (Chemviron Carbon, UK)	57.47
AC Rice husk	50
Modified silica	45.8
Saw dust-walnut	36.98
Banana peel	21
Wood sawdust (raw)	5.92
Blast furnace sludge	2.1

3.4. Comparison of MB removal efficiency before and after surface functionalization

According to the existing literatures, the isoelectric point of maghemite and magnetite is pH 3.3–6.7 and pH 6.5–6.8, respectively [46,47]; hence, while dispersing in deionized water (~pH 7), both of the nanospheres and nanorods are negatively charged. After the attachment of very low molecular weight of cationic polyelectrolyte PDADMAC, the NPs experienced both charge reversal and the hydrodynamic diameter increment (Table 1). These results present very strong evidence suggesting the likely success in surface functionalization of NPs by PDADMAC. The drastic reduction of nanorod's average hydrodynamic diameter from 1075.4 ± 35.9 nm to 319.8 ± 3.3 together with the narrowing of its size distribution as indicated by the decrement in standard deviation of hydrodynamic diameter measurement confirmed the formation of more colloidally stable NPs dispersion; whereas, the slight increment of nanosphere's hydrodynamic diameter, with the degree of increment approaching the hydrodynamic diameter of the PDADMAC molecule, provides another mean (in addition to the zeta potential measurement) to confirm the successful surface functionalization of nanosphere [48].

The employment of PDADMAC modified nanorods and nanospheres PVDF microcapsules for MB removal had given extremely different performance compared to those NPs-PVDF microcapsules without gone through surface modification. Surface functionalized nanorod-PVDF microcapsule gives the best removal efficiency for all MB discoloration experiments in this work. According to Fig. 8a, surface functionalization has significantly enhanced the MB removal performance of nanorod-PVDF microcapsule from 64% to 86%. We hypothesized that with the present of the PDADMAC layer, the TODA nanorods are more readily to be dispersed in suspension and achieved better colloid stability (without aggregation) prior and during the synthesis of microcapsule. It is this extra electrosteric hindrance layer that fights against other agglomeration induced interactions, mainly originated from magnetic dipole–dipole and van der Waals interacting potentials, and prevents TODA nanorods from aggregation and forming NP clusters [49]. The immediate consequence of having stable colloid dispersion of TODA nanorod is the increment of their surface-to-volume ratio while encapsulated within the PVDF network. The outcome is pretty straightforward, with more available active site for MB degradation, the removal efficiency of this species of microcapsules improved quite significantly.

In contrast to the observations made on nanorod, the MB removal efficiency of nanosphere was slightly reduced after surface functionalized by PDADMAC as shown in Fig. 8b due to the electrostatic repulsion between the PDADMAC layer and MB molecules. Since, the poly (vinyl pyrrolidone) decorated Sigma nanospheres already dispersed pretty well during the process of microcapsules making the introduction of extra PDADMAC layer has no significant colloid stability improvement. In fact this layer has obviously magnifying the charged barrier resulting positively charged MB [34,50] hardly to approach the nanosphere due to electrostatic repulsion with the positively charged PDADMAC [51]. Combination of these two disputing observations lead us to believe that by achieving better colloidal stability for the magnetic NPs employed is crucial to further boost the performance of this NPs-polymeric hybrid nanomaterial for pollutant removal.

To further investigate the role of surface functionalization of NPs employed in dictating the MB removal efficiency of NPs-PVDF microcapsule, we introduced PDADMAC with different molecular weight onto the TODA nanorod before its entrapment into PVDF matrix. As shown in Fig. 9, NPs-PVDF microcapsule with its particles decorated by very low M_w PDADMAC outperformed all other species of NPs-PVDF microcapsule tested. Comparing the MB removal efficiency of very low M_w and low M_w PDADMAC coated nanorod-PVDF microcapsules, we found out that even though the low M_w PDADMAC is equally effective in stabilizing TODA nanorods (see Table 1), but due to its larger molecular size, the electrostatic barrier experienced by approaching MB molecule has also increased. This in turn has retarded the MB removal capability of low M_w PDADMAC decorated nanorods. As for medium M_w PDADMAC is concerned, from DLS measurements in Table 1, this polyelectrolyte has failed to redisperse the TODA nanorod mostly due to the bridging flocculation [52]. The colloid instability of this species of nanorod, together with the thicker layer of electrosteric barrier formed, would be the main contributing factors toward the poor MB performance witnessed in Fig. 9. Ironically, the MB removal

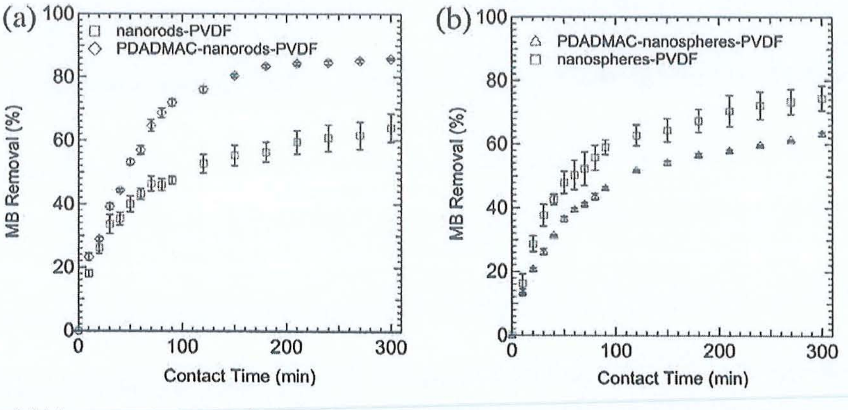

Fig. 8. Percent MB (with 100 ppm initial concentration) removal achieved by using NPs-PVDF microcapsules, before and after surface functionalization of (a) TODA nanorods and (b) Sigma nanospheres, by very low molecular weight PDADMAC.

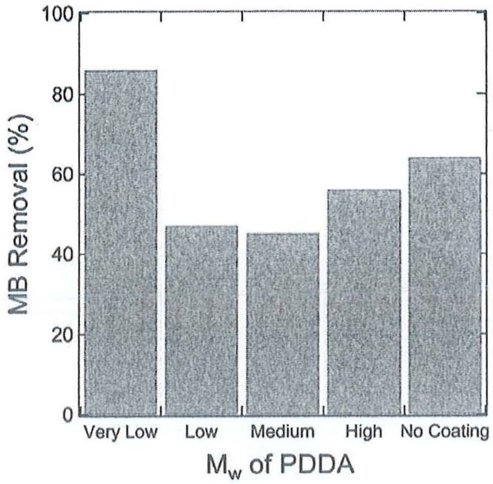

Fig. 9. MB removal capability of nanorods-PVDF microcapsule with the TODA nanorods surface functionalized by PDADMAC molecules of different molecular weight. The molecular weight of PDADMAC employed are $M_w < 100{,}000$ (very low molecular weight), $M_w \sim 100{,}000–200{,}000$ (low molecular weight), $M_w \sim 200{,}000–350{,}000$ (medium molecular weight) and $M_w \sim 400{,}000–500{,}000$ (high molecular weight).

efficiency has improved with the use of high M_w PDADMAC, compared to both low and medium M_w PDADMAC, for surface functionalization of TODA nanorods after its insertion into PVDF polymer. Since the hydrodynamic diameter of this polyelectrolyte at 191.7 ± 41.6 nm is very close to the size of individual TODA nanorods [53], so instead of surface modified the particles, the nanorods and high M_w PDADMAC entangled together and forming a micron sized matrix with its diameter reaching ~1677 nm. This structural should be loosely packed and is very likely to impose less electrostatic hindrances which further allowed the MB molecules to diffuse through its inner matrix. Nevertheless, the results presented in Fig. 9 has revealed a very complex interplay of factors, involving electrostatic interaction, molecular sizes, colloidal stability of particles, has to be taken into account in synthesizing surface functionalized NPs-polymeric microcapsules tailored towards specific environmental engineering applications.

4. Conclusion

We have successfully synthesized magnetic NPs-polymeric microcapsules and demonstrated the engineering applications of this hybrid material on removing methylene blue (MB) from water resources. Both of the nanorods-PVDF and nanospheres-PVDF microcapsule has the potential to be regenerated and can be employed for multiple cycle of MB removal while still retaining their magnetic response. For fresh batch of NPs-PVDF microcapsule, the removal of MB from its surrounding media is basically driven by both entrapment and catalytic degradation. In the following recycling processes, catalytic degradation should play a more dominant role. The inherent catalytic and magnetic properties exhibited by Fe^0/iron oxides NPs-PVDF microcapsules, compared to conventional activated carbon based absorbent, make them an attractive candidate to remove cationic dye from aqueous environment. After surface functionalized with very low cationic polyelectrolyte PDADMAC, the MB removal efficiency of NPs-PVDF microcapsule improved for nanorods and deteriorated for nanosphere. These scenarios are related to the colloid stability of the particles employed in which the obvious enhancement of MB removal capacity can only be witnessed in nanorods with bad initial dispersibility. However, the increment of molecular weight of PDADMAC suppressed the MB removal capacity of nanorods-PVDF microcapsule due to higher electrostatic barrier between surface functionalized nanorods with MB. The true advantages of using this hybrid materials for environmental applications compared to freely suspended nanoparticles are (i) the risk associated to nanotoxicity has been greatly reduced and (ii) the catalytic and magnetic stability achieved after the encapsulation of Fe^0/iron oxide nanoparticles into polymeric network.

Acknowledgments

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Tuan,

Perincian Geran Penyelidikan Tajaan Agensi Luar – Projek Baru
- **Penaja : NIPPON SHEET GLASS FOUNDATION (NSG)**
- **Tajuk Projek : *'Design and Synthesis of Magnetic Nanoparticles Augmented Microcapsule for Removing Heavy Metal from Water Resources'***
- **No. Akaun : 304/PJKIMIA/6050207/N100**

Dengan hormatnya perkara di atas dirujuk.

2. Sukacita bersama ini disampaikan borang perincian geran berjumlah **RM18,048.00** yang diluluskan oleh pihak universiti untuk bayaran projek penyelidikan tuan ***'Design and Synthesis of Magnetic Nanoparticles Augmented Microcapsule for Removing Heavy Metal from Water Resources'***. Harap maklum, selaras dengan keputusan Jawatankuasa Eksekutif Naib Canselor pada 17 Mac 2005 yang mana telah dimaklumkan kepada semua melalui memo RCMO bertarikh 13 Julai 2005 bahawa 2.5% atau **RM451.20** dikenakan caj perkhidmatan.

Sekian, terima kasih.

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Tuan,

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[word 1:surat ucapan terima kasih]TPHEA

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